CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Syntheses of Seven-Membered Rings: Ru-Catalyzed Intramolecular [5 + 2] Cycloadditions

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General Information

All experiments were carried out in flame or oven-dried glassware under an atmosphere of dry argon with magnetic stirring. Anhydrous solvents were transferred by oven-dried syringe or cannula. Dichloroethane was distilled from calcium hydride. Acetone was distilled from calcium sulfate. Anhydrous DMF was purchased from Aldrich and used as received. Dichloromethane, ether, toluene, and acetonitrile were dried by passing through a column of activated alumina[1] using a Solv-Tek solvent purification system. $[CpRu(CH_3CN)_3]PF_6$,[2] Ru(cod)(cot),[3] and $Ru(ind)_2$[4] were prepared according to procedures described in the literature. All other reagents were of commercial grade and were either recrystallized or distilled before use following the guidelines of Perrin and Armarego.[5]

Flash chromatography was performed with EM Reagent silica gel 60 (230-400 mesh) using the method of Still.[6] Analytical thin layer chromatography (TLC) was performed with EM Reagent 0.25 mm silica gel 60-F commercial silica gel plates. Visualization was accomplished with UV light and potassium permanganate stain, followed by heating.

Melting points were determined on a Thomas-Hoover melting point apparatus in open capillaries and are uncorrected. Infrared spectra were obtained as neat films on NaCl plates, or as KBr-pellets for reactions where a solid was obtained, with a Perkin-Elmer Paragon 500 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). M-H-W Laboratories, Phoenix, Arizona performed combustion analyses. High resolution mass spectra (HRMS) were recorded by the Mass Spectrometer Facility of the School of Pharmacy, University of California, San Francisco. Accurate masses are reported for the molecular ion (M^+) or a suitable fragment ion. Reported mass values are within error limits of $\pm$ 13 millimass units.

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on Varian Gemini GEM-200 (200 MHz), Gemini GEM-300 (300 MHz), INova UI-400 (400 MHz), or INova UI-500 (500 MHz) spectrometers. The chemical shifts are reported in ppm with $CDCl_3$ (δ=7.24) or TMS (δ=0.00) as the internal standard unless otherwise noted. ^{13}C NMR spectra were acquired on Gemini GEM-300 (75 MHz) or INova UI-500 (125 MHz) spectrometers in $CDCl_3$ using TMS (δ=0.00) or $CDCl_3$ (δ=77.0) as an internal standard.

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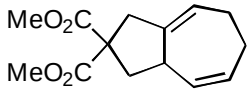
[1] Pangborn, A.B.; Giardello, M.A.; Grubbs, R.H.; Rosen, R.K.; Timmers, F.J. *Organometallics* **1996**, *15*, 1518.
[2] Trost, B.M.; Older, C.M. *Organometallics* **2002**, *21*, 2544.
[3] Frosin, K.M.; Dahlenburg, L. *Inorg. Chim. Acta* **1990**, *167*, 83.
[4] Crossley, N.S.; Green, J.C.; Nagy, A.; Stringer, G. *J. Chem. Soc. Dalton Trans.* **1989**, 2139.
[5] Perrin, D.D.; Armarego, W.L. *Purification of Laboratory Chemicals*; 3rd ed., Pergamon Press, Oxford. 1988.
[6] Still, W.C.; Kahn, M.; Mitra A. *J. Org. Chem.*. **1978**, *43*, 2923.

Part I:
Cycloaddition Reactions:

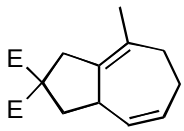
General Procedure: Ruthenium Catalyzed [5+2] Cycloadditions.
To a oven-dried test tube is added 10% $[CpRu(CH_3CN)_3]PF_6$ and the flask purged with Ar three times. A solution of eneyne-cyclopropane in freshly distilled acetone is added via cannula and the solution stirred under Ar at rt until TLC shows the reaction is complete. The solvent is removed *in vacuo*, and the residue purified by flash chromatography on silica gel.

Ruthenium [5+2] Cycloaddition Reactions



6a

Table 1, entry 1:
2,2-Bis(methoxycarbonyl)-1,2,3,3a,6,7-hexahydroazulene (**6a**): To a test tube containing $CpRu(CH_3CN)_3PF_6$ (6 mg, 0.014 mmol) was added a solution of vinylcyclopropane **5a** (35 mg, 0.139 mmol) in acetone (0.7 mL) and the resulting orange solution stirred at room temperature for 2 h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 6:1 petroleum ether:diethyl ether to afford **6a** (29 mg, 83%) as a colorless liquid.
IR (film): 3004, 2954, 2846, 1736, 1435, 1253 1202, 1163, 1074 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.71 (m, 1H), 5.65 (m, 1H), 5.52 (br d, *J* = 11 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.69 (m, 1H), 2.98 (dd, *J* = 16.4 and 1.3 Hz, 1H), 2.95 (ddd, *J* = 16.4, 2.2 and 1.6 Hz, 1H), 2.68 (ddd, *J* = 12.5, 8.4 and 1.1 Hz, 1H), 2.35 (m, 2H), 2.09 (m, 2H), 2.04 (dd, *J* = 12.5 and 11.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.0, 171.9, 142.4, 132.0, 130.2, 122.2, 58.5, 52.7, 52.6, 41.4, 41.2, 39.6, 26.2, 25.7; HRMS (EI+) Calc'd for $C_{14}H_{18}O_4$ $[M]^+$: 250.1205. Found: 250.1205.

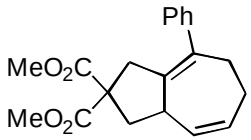


6b

Table 1, Entry 2:
2,2-Bis(methoxycarbonyl)-8-methyl-1,2,3,3a,6,7-hexahydroazulene (**6b**):[7] To a flask containing $CpRu(CH_3CN)_3PF_6$ (8 mg, 0.019 mmol) was added a solution of **5b** (50 mg, 0.19 mmol) in acetone (2 mL) and the resulting orange solution stirred at room temperature for 3 h. The reaction mixture was directly chromatographed eluting with 10% diethyl ether: petroleum ether to afford **6b** (41 mg, 0.16 mmol, 82%).
IR (film): 2953s, 2853s, 1737s, 1434s, 1255s, 1230s, 1201s, 1164s, 1080s, 950s, 887m cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.62 (m, 1H); 5.44 (d, *J*=11 Hz, 1H), 3.73 (s, 3H), 3.65 (m, 1H), 3.00 (d, *J*=16.5 Hz, 1H), 2.85 (d, *J*=16.5 Hz, 1H), 2.68 (m, 1H), 2.55 (m, 1H), 2.24 (m, 1H), 2.05 (m, 1H), 1.95 (m, 1H), 1.86 (m, 1H), 1.25 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 172.1, 172.0,

[7] See: Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc.* **1995**, *112*, 4720.

135.3, 131.9, 129.6, 129.5, 58.4, 52.7, 52.6, 41.8, 39.7, 39.1, 32.4, 25.9, 21.2; HRMS (EI+) Calc'd for $C_{15}H_{20}O_4$ $[M]^+$: 264.1362. Found: 264.1350.

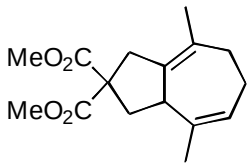


6c

Table 1, entry 3:

2,2-Bis(methoxycarbonyl)-8-phenyl-1,2,3,3a,6,7-hexahydroazulene (**6c**): To a test tube containing $CpRu(CH_3CN)_3PF_6$ (8 mg, 0.018 mmol) was added a solution of vinylcyclopropane **5c** (60 mg, 0.184 mmol) in acetone (0.9 mL) and the resulting orange solution stirred at room temperature for 2 h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 5% diethyl ether:petroleum ether to afford **6c** (49 mg, 82%) as a colorless liquid.

IR (film): 3005, 2954, 2845, 1733, 1435, 1256 1203, 1173, 1074, 764, 703 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 7.9 and 7.1 Hz, 2H), 7.24 (m, 3H), 5.64 (m, 1H), 5.47 (ddd, *J* = 11.2, 3.8, and 2.0 Hz, 1H), 3.89 (m, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.03 (dt, *J* = 16.3 and 2.6 Hz, 1H), 3.01 (m, 1H), 2.92 (d, *J* = 16.3 Hz, 1H), 2.77 (ddd, *J* = 12.6, 8.4 and 1.9 Hz, 1H), 2.36 (m, 1H), 2.28 (m, 2H), 2.04 (dd, *J* = 12.6 and 10.2 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 171.8, 171.7, 143.5, 140.2,135.2, 130.8, 129.5, 128.1, 127.7, 126.2, 58.8, 52.7, 52.6, 41.6, 40.1, 32.7, 26.7; Anal. Calc'd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 74.00; H, 6.67.

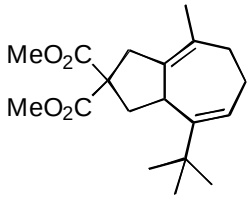


6d

Table 1, entry 4:

2,2-Bis(methoxycarbonyl)-4,8-dimethyl-1,2,3,3a,6,7-hexahydroazulene (**6d**): To a test tube containing $CpRu(CH_3CN)_3PF_6$ (7 mg, 0.016 mmol) was added a solution of vinylcyclopropane **5d** (45 mg, 0.161 mmol) in acetone (0.8 mL) and the resulting orange solution stirred at room temperature for 1 h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 6:1 petroleum ether:diethyl ether to afford **6d** (39 mg, 87%) as a colorless liquid.

IR (film): 2953, 1737, 1434, 1270 1202, 1166 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.61 (m, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.71 (m, 1H), 3.07 (d, *J* = 16.5 Hz, 1H), 2.79 (d, *J* = 16.5 Hz, 1H), 2.64 (ddd, *J* = 12.5, 7.5 and 2.2 Hz, 1H), 2.35 (m, 1H), 2.20 (m, 1H), 2.15 (t, *J* = 12.5 Hz, 1H), 2.02 (m, 1H), 1.93 (m, 1H), 1.74 (s, 3H), 1.63 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.3, 172.0, 138.2, 132.3, 129.4, 125.8, 57.7, 52.8, 52.7, 42.3, 39.5, 38.6, 32.5, 25.3, 22.6, 22.0; Anal. Calc'd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.09; H, 7.81.

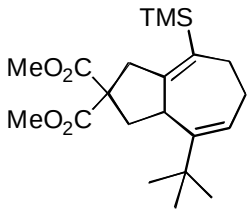


6e

Table 1, entry 5:

4-*tert*-Butyl-8-methyl-3,3a,6,7-tetrahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (**6e**): Malonate **5e** (19.0 mg, 0.059 mmol) and $[CpRu(CH_3CN)_3]PF_6$ (2.6 mg, 0.006 mmol) were dissolved in 0.6 mL of dichloroethane and stirred under Ar at room temperature for 24 h. The solvent was removed *in vacuo* and the residue purified by flash chromatography (silica gel, 3:1 petroleum ether:diethyl ether) to afford cycloadduct **6e** (15.8 mg, 0.049 mmol, 83%).

R_f=0.49 (3:1 petroleum ether:ether); IR (film): 2954, 2922, 2868, 1737, 1433, 1365, 1327, 1257, 1198, 1166, 1085, 953 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.76 (t, J=7.2 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.70 (m, 1H), 2.85 (s, 2H), 2.71 (dd, J=12.0, 7.5 Hz, 1H), 2.31 (m, 2H), 2.04 (m, 1H), 1.84 (m, 1H), 1.73 (m, 1H), 1.57 (s, 3H), 1.08 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 172.54, 172.49, 150.3, 132.4, 128.3, 123.6, 57.9, 52.7, 52.6, 42.5, 39.4, 38.6, 36.3, 32.4, 30.6, 30.3, 25.7, 22.7; Anal. Calc'd for $C_{19}H_{28}O_4$: C, 71.22; H, 8.81. Found: C, 71.38; H, 8.67.

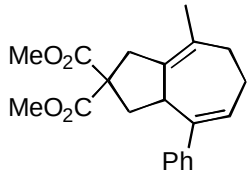


6f

Table 1, entry 6:

4-tert-Butyl-8-trimethylsilanyl-3,3a,6,7-tetrahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (**6f**): Malonate **5f** (15.2 mg, 0.040 mmol) and $[CpRu(CH_3CN)_3]PF_6$ (4.0 mg, 0.010 mmol) were dissolved in 0.4 mL of dichloroethane and stirred under Ar at room temperature for 24 h. The solvent was removed *in vacuo* and the residue purified by flash chromatography (silica gel, 3:1 petroleum ether:diethyl ether) to afford cycloadduct **6f** (14.5 mg, 0.038 mmol, 95%).

R_f=0.55 (3:1 petroleum ether:ether); IR (film): 2954, 2180, 1737, 1433, 1252, 1198, 1162, 1071, 836, 754 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.76 (t, J=6.3 Hz, 1H), 3.79 (m, 1H), 3.72 (s, 3H), 3.05 (dd, J=12.6, 6.9 Hz, 2H), 2.87 (m, 2H), 2.68 (dd, J=12.6, 8.4 Hz, 1H), 2.35 (m, 2H), 2.05 (m, 2H), 1.08 (s, 9H), 0.08 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 172.4, 172.3, 149.4, 148.1, 133.2, 124.1, 58.0, 52.70, 52.65, 44.9, 41.7, 39.0, 30.4, 29.2, 26.8, 22.9, -0.04; Anal. Calc'd for $C_{21}H_{34}O_4Si$: C, 66.62; H, 9.05. Found: C, 66.81; H, 8.96.

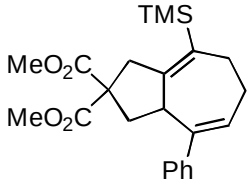


6g

Table 1, entry 7:

8-Methyl-4-phenyl-3,3a,6,7-tetrahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (**6g**): Malonate **5g** (9.8 mg, 0.029 mmol) and $[CpRu(CH_3CN)_3]PF_6$ (2.5 mg, 0.0058 mmol) were dissolved in 0.5 µL H_2O and 0.30 mL dichloroethane and stirred under Ar at room temperature for 24 h. The solvent was removed *in vacuo* and the residue purified by flash chromatography (silica gel, 3:1 petroleum ether:diethyl ether) to afford cycloadduct **6g** (8.2 mg, 0.024 mmol, 84%).

R_f=0.50 (3:1 petroleum ether:ether); IR (film): 2953, 2854, 1752, 1434, 1265, 1203, 1165, 1070, 759, 703 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.25 (m, 3H), 7.16 (m, 2H), 5.70 (m, 1H), 4.15 (m, 1H), 3.72 (s, 3H), 3.61 (s, 3H), 2.93 (d, J=16.2 Hz, 2H), 2.49 (m, 2H), 2.35 (m, 1H), 2.20 (m, 2H), 1.93 (m, 1H), 1.70 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 172.2, 172.0, 144.8, 142.5, 133.2, 130.8, 130.6, 127.8, 127.5, 126.0, 57.6, 52.8, 52.6, 42.1, 41.2, 39.4, 32.4, 26.5, 21.7; Anal. Calc'd for $C_{19}H_{28}O_4$: C, 74.09; H, 7.11. Found: C, 73.94; H, 7.00.

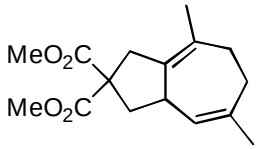


6h

Table 1, entry 8:

4-Phenyl-8-trimethylsilanyl-3,3a,6,7-tetrahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (**6h**): Malonate **5h** (10.1 mg, 0.025 mmol) and $[CpRu(CH_3CN)_3]PF_6$ (3.1 mg, 0.0076 mmol) were dissolved in 0.25 mL dichloroethane and stirred under Ar at room temperature for 24 h. The solvent was removed *in vacuo* and the residue purified by flash chromatography (silica gel, 3:1 petroleum ether:diethyl ether) to afford cycloadduct **6h** (7.6 mg, 0.019 mmol, 75%).

R_f=0.43 (3:1 petroleum ether:ether); IR (film): 2953, 2180, 1738, 1629, 1435, 1251, 1198, 1163, 1077, 838, 734, 703 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.20 (m, 5H), 5.61 (m, 1H), 4.34 (m, 1H), 3.72 (s, 3H), 3.62 (s, 3H), 3.01 (d, J=15.9 Hz, 2H), 2.59 (m, 2H), 2.32 (m, 2H), 2.18 (m, 2H), 0.16 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 171.8, 171.7, 152.3, 145.3, 140.2, 135.6, 131.1, 127.8, 127.4, 125.9, 58.2, 52.7, 52.6, 43.1, 41.7, 40.7, 28.8, 28.5, -0.3; Anal. Calc'd for $C_{23}H_{30}O_4Si$: C, 69.31; H, 7.59. Found: C, 69.17; H, 7.50.

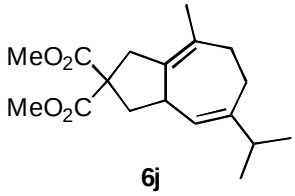


6i

Table 1, entry 9:

2,2-Bis(methoxycarbonyl)-5,8-dimethyl-1,2,3,3a,6,7-hexahydroazulene (**6i**): To a test tube containing $CpRu(CH_3CN)_3PF_6$ (3 mg, 0.007 mmol) was added a solution of vinylcyclopropane **5i** (20 mg, 0.072 mmol) in acetone (0.7 mL) and the resulting orange solution stirred at 50 ºC for 2 h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 20:1 petroleum ether: diethyl ether to afford **6i** (15 mg, 75%) as a colorless liquid.

IR (film): 2955, 1737, 1434, 1377, 1260 1202, 1166, 1073 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.29 (m, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.52 (m, 1H), 3.03 (d, *J* = 16.4 Hz, 1H), 2.86 (d, *J* = 16.4 Hz, 1H), 2.64 (ddd, *J* = 12.7, 8.0 and 2.0 Hz, 1H), 2.37 (m, 2H), 1.98 (dd, *J* = 12.7 and 11.5 Hz, 1H), 1.96 (m, 2H), 1.69 (t, *J* = 1.6 Hz, 3H), 1.66 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.2, 172.1, 137.5, 134.8, 128.6, 126.6, 58.4, 52.7, 52.6, 41.9, 39.2, 31.8, 30.8, 25.1, 21.2; HRMS (EI+) Calc'd for $C_{16}H_{22}O_4$ $[M]^+$: 278.1283. Found: 278.1243.

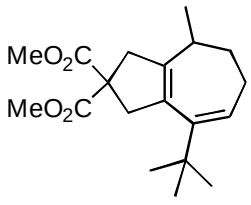


6j

Table 1, entry 10:

5-*iso*-Propyl-8-methyl-3,3a,6,7-tetrahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (**6j**): To a solution of malonate **5j** (80 mg, 0.26 mmol) in 1 mL of acetone under argon was added $[CpRu(CH_3CN)_3]PF_6$ (11 mg, 0.026 mmol). The mixture was stirred at room temperature for 2 h. Without workup, the mixture was purified by flash chromatography (silica gel, 5% to 10% of diethyl ether in petroleum ether) to afford cycloadduct **6j** (70 mg, 0.23 mmol, 88%) as a yellow oil.

R_f=0.23 (1:1 petroleum ether:ether); IR (film): 2958s, 1738s, 1435w, 1265s, 1202m, 1165m, 1076w cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.31 (s, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.50 (bs, 1H), 3.02 (d, *J*=16.8 Hz, 1H), 2.83 (d, *J*=16.8 Hz, 1H), 2.64 (ddd, *J*=2.1, 8.1, 12.6 Hz, 1H), 2.53 (t, *J*=13.5 Hz, 1H), 2.19 (m, 2H), 2.00 (m, 3H), 1.56 (s, 3H), 0.99 (s, 3H), 0.96 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 172.3, 147.9, 133.3, 127.9, 125.1, 65.8, 58.3, 41.7, 39.5, 39.1, 35.8, 32.7, 27.3, 21.4, 21.2, 15.2; HRMS (EI+) Calc'd for $C_{16}H_{23}O_2$ $[M - CO_2CH_3]^+$: 247.1698. Found: 247.1694.

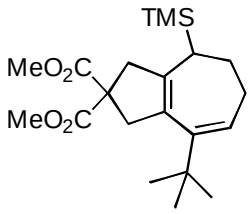


6k

Table 1, entry 11:

8-*tert*-Butyl-4-methyl-3,4,5,6-tetrahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (**6k**): A solution of Ru(cod)(cot) (0.56 mg, 1.3 x 10^{-3} mmol) in 0.1 mL of CH_2Cl_2 under Ar was treated with 0.5 µL of a 5.5 M solution of HPF_6 in water (3 x 10^{-3} mmol). The yellow solution immediately turned orange-brown. This solution was stirred 10 min, before malonate **5k** (4.2 mg, 0.013 mmol) was added and the solution stirred at room temperature for 12 h. The solvent was removed *in vacuo* and the residue purified by flash chromatography (silica gel, 3:1 petroleum ether:diethyl ether) to afford cycloadduct **6k** (3.1 mg, 0.010 mmol, 75%).

R_f=0.47 (3:1 petroleum ether:ether); IR (film): 2955, 2258, 1738, 1436, 1364, 1284, 1202, 1116, 1089, 1071, 913, 736 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.24 (t, J=6.6 Hz, 1H), 3.72 (s, 6H), 3.39 (t, J=7.2 Hz, 2H), 2.80 (d, J=2.4 Hz, 2H), 2.26 (q, J=6.9 Hz, 1H), 2.08 (m, 2H), 1.89 (m, 2H), 1.73 (s, 3H), 1.00 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 171.1, 170.9, 147.3, 130.9, 128.8, 119.2, 57.2, 57.1, 52.6, 38.6, 36.6, 29.7, 29.3, 22.7, 22.4; Anal. Calc'd for $C_{19}H_{28}O_4$: C, 71.22; H, 8.81. Found: C, 70.72; H, 8.68.

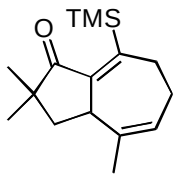


6l

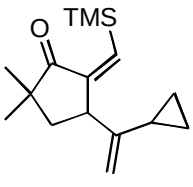
Table 1, entry 12:

8-tert-Butyl-4-trimethylsilanyl-3,4,5,6-tetrahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (**6l**): A solution of Ru(ind)$_2$ (0.8 mg, 2.4 x 10^{-3} mmol) in 0.2 mL of CH_2Cl_2 under argon was treated with 0.5 µL of a 5.5 M solution of HPF_6 in water (3 x 10^{-3} mmol). The yellow solution immediately turned orange-brown. This solution was stirred 10 min, before malonate **5l** (9.1 mg, 0.024 mmol) was added and the solution stirred at room temperature for 12 h. The solvent was removed *in vacuo* and the residue purified by flash chromatography (silica gel, 3:1 petroleum ether:diethyl ether) to afford cycloadduct **6l** (6.6 mg, 0.017 mmol, 73%).

R_f=0.55 (3:1 petroleum ether:ether); IR (film): 2956, 2871, 2180, 1738, 1436, 1363, 1251, 1200, 1029, 845, 761 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.25 (m, 1H), 3.73 (s, 6H), 3.39 (t, J=7.2 Hz, 2H), 2.87 (s, 2H), 2.40 (m, 1H), 2.08 (m, 2H), 1.91 (m, 2H), 1.01 (s, 9H), 0.09 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.6, 170.5, 149.7, 149.1, 147.2, 119.4, 57.3, 57.2, 52.7, 52.6, 36.8, 36.7, 31.8, 30.2, 29.4, 22.4, 1.0, -0.1; Anal. Calc'd for $C_{21}H_{34}O_4Si$: C, 66.62; H, 9.05. Found: C 66.40; H, 8.99.



6m



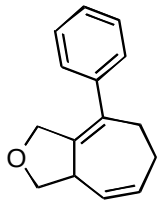
6m'

Table 1, entry 13:

2,2,5-Trimethyl-8-trimethylsilyl-3,3a,6,7-hexahydroazulen-1-one (**6m**): To a test tube containing $CpRu(CH_3CN)_3PF_6$ (5 mg, 0.012 mmol) was added a solution of vinylcyclopropane **5m** (a 2.4:1 mixture of *E*- and *Z*-alkenes) (28 mg, 0.107 mmol) in acetone (0.5 mL) and the resulting orange solution stirred at room temperature for 2 h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 15:1 petroleum ether:diethyl ether to afford 3.7:1 mixture of **6m**:**6m'** (41 mg, 82%) as a colorless liquid. The ratio of **6m**:**6m'** was determined by ^{1}H-NMR integration of one of the olefinic protons: for **6m** a multiplet at 5.48 ppm (1H) and for **6m'** a doublet at 6.07 ppm (1H).

IR (film): 2960, 1783, 1593, 1458, 1244, 1134, 1102, 1075, 842 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.48 (m, 1H), 3.81 (m, 1H), 2.48 (m, 2H), 2.22 (m, 1H), 1.97 (dd, *J* = 12.5 and 8.3 Hz, 1H), 1.90 (m, 2H), 1.66 (d, *J* = 1.2 Hz, 1H), 1.03 (s, 3H), 0.94 (s, 3H), 0.08 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 210.1, 161.5, 135.7, 126.5, 108.6, 128.0, 41.5, 40.7, 40.2, 31.7, 26.0, 24.0, 23.2, -0.2; HRMS (EI+) Calc'd for $C_{16}H_{26}OSi$ $[M]^+$: 262.1753. Found: 262.1746.

Additional signals for **6m'**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.07 (d, J = 2.7 Hz, 1H), 4.68 (s, 1H), 4.64 (t, *J* = 1.1 Hz, 1H), 4.68 (m, 1H), 3.45 (td, *J* = 9.6 and 2.8 Hz, 1H), 2.53 (dt, *J* = 10.5 and 2.5 Hz, 1H), 1.08 (s, 3H), 1.01 (s, 3H), 0.59 (m, 2H), 0.48 (m, 1H), 0.30 (m, 1H), 0.08 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 147.3, 143.2, 48.6, 41.5, 24.6, 23.5, 12.8, 8.4, 6.4, -0.8.

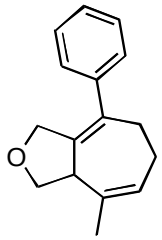


6n

Table 1, entry 14:

8-Phenyl-3,3a,6,7-tetrahydro-1H-cyclohepta[c]furan (**6n**):[7] To a test tube containing $CpRu(CH_3CN)_3PF_6$ (3 mg, 0.007 mmol) was added a solution of vinylcyclopropane **5n** (13 mg, 0.061 mmol) in acetone (0.6 mL) and the resulting orange solution stirred at room temperature for 4 h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 5% diethyl ether:petroleum ether to afford **6n** (10 mg, 77%) as a clear film.

IR (film): 3010, 2945, 1600, 1492, 1359, 1103, 1054, 935, 763 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 8.1 and 7.6 Hz, 2H), 7.25 (tt, *J* = 7.6 and 1.5 Hz, 1H), 7.19 (dd, *J* = 8.1 and 1.5 Hz 2H), 5.75 (m, 1H), 5.48 (ddd, *J* = 11.2, 3.4 and 1.9 Hz, 1H), 4.37 (dt, *J* = 13.4 and 2.1 Hz, 1H), 4.33 (d, *J* = 13.4 Hz, 1H), 4.27 (t, *J* = 8.4 Hz, 1H), 3.95 (m, 1H), 3.61 (t, *J* = 8.4 Hz, 1H), 3.02 (m, 1H), 2.49-2.20 (m, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 142.6, 140.8, 132.4, 130.6, 128.0, 127.8, 126.9, 126.4, 74.8, 71.2, 41.7, 32.2, 26.8.

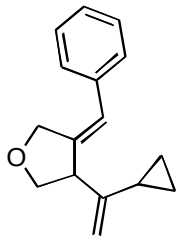


6o

Table 1, entry 15:

4-Methyl-8-phenyl-3,3a,6,7-tetrahydro-1*H*-cyclohepta[c]furan (**6o**):[7] To a test tube containing $CpRu(CH_3CN)_3PF_6$ (10 mg, 0.023 mmol) was added a solution of vinylcyclopropane **5o** (50 mg, 0.221 mmol) in acetone (1.0 mL) and the resulting orange solution stirred at room temperature for 2h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 5% diethyl ether:petroleum ether to afford 6.2:1 mixture of **6o**:**6p** (41 mg, 82%) as a colorless liquid. The ratio of **6o**:**6p** was determined by ^{1}H-NMR integration of one of the olefinic protons: for **6o** a multiplet at 5.63 ppm (1H) and for **6p** a quartet at 6.36 ppm (1H).

IR (film): 3021, 2940, 2850, 1492, 1442, 1085, 936, 761, 700 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 8.2 and 7.6 Hz, 2H), 7.24 (tt, *J* = 7.6 and 1.3 Hz, 1H), 7.19 (dd, *J* = 8.2 and 1.3 Hz, 2H), 5.63 (m, 1H), 4.25 (t, *J* = 1.4 Hz, 2H), 4.24 (dd, *J* = 11.0 and 8.6 Hz, 1H), 3.95 (m, 1H), 3.81 (dd, *J* = 9.2 and 8.6 Hz, 1H), 2.72 (m, 1H), 2.43 (m, 1H), 2.37 (m, 1H), 2.26 (m, 1H), 1.77 (d, *J* = 1.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 143.5, 137.8, 134.7, 128.3, 128.0, 127.1, 126.5, 126.2, 72.4, 71.7, 44.9, 32.5, 26.4, 22.5; HRMS (EI+) Calc'd for $C_{16}H_{18}O$ $[M]^+$: 226.1358. Found: 226.1360.



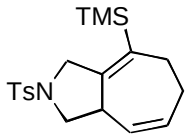
6p

Table 1, entry 16:

3-Benzylidene-4-(1-cyclopropylvinyl)-dihydrofuran-2-one (**6p**)**:** To a test tube containing $CpRu(CH_3CN)_3PF_6$ (8 mg, 0.018 mmol) was added a solution of vinylcyclopropane **5p** (40 mg, 0.177 mmol) in acetone (0.9 mL) and the resulting orange solution stirred at room temperature 2h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 5% diethyl ether: petroleum ether to afford 1:14 mixture of **5o**:**5p** (31 mg, 78%) as a colorless liquid. The ratio of **5o**:**5p** was determined by ^{1}H-NMR integration of one of the olefinic protons: for **5o** a multiplet at 5.63 ppm (1H) and for **5p** a quartet at 6.36 ppm (1H).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.37 (t, *J* = 7.3 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.3 Hz, 2H), 6.36 (q, *J* = 2.4 Hz, 1H), 4.86 (s, 1H), 4.75 (s, 1H), 4.68 (m, 1H), 4.07 (t, *J* = 8.6 Hz, 1H), 3.98 (dd, *J* = 8.6 and 7.2 Hz, 1H), 3.67 (br t, *J* = 6.9 Hz, 1H), 1.27 (m, 1H), 0.66 (m, 2H), 0.57 (m, 1H), 0.39 (m, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 143.6, 137.4, 133.3, 128.5, 128.2,

126.7, 122.1, 108.7, 72.0, 70.7, 34.2, 8.7, 7.2. HRMS (EI+) Calc'd for $C_{16}H_{17}O$ [M – H]$^+$: 225.1279. Found: 225.1295.

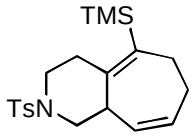


6q

Table 1, entry 17:

***N*-(4-Methylbenzenesulfonyl)-8-(trimethylsilyl)-1,2,3,3a,6,7-hexahydro-cyclohepta[c]pyrrole** (**6q**): To a test tube containing $CpRu(CH_3CN)_3PF_6$ (3 mg, 0.007 mmol) was added a solution of vinylcyclopropane **5q** (25 mg, 0.069 mmol) in acetone (0.7 mL) and the resulting orange solution stirred at room temperature for 2 h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 6:1 petroleum ether:diethyl ether to afford **6q** (21 mg, 84%) as a clear film.

IR (film): 2953, 2922, 2850, 1596, 1350, 1248, 1161, 1093, 1027, 836 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 5.51 (m, 1H), 5.18 (ddd, *J* = 11.4, 4.0 and 2.0 Hz, 1H), 3.93 (d, *J* = 13.1 Hz, 1H), 3.92 (m, 1H), 3.64 (m, 2H), 2.72 (dd, *J* = 9.2 and 8.4 Hz, 1H), 2.56 (br t, *J* = 13.4 Hz, 1H), 2.47 (s, 3H), 2.21 (m, 1H), 2.12 (m, 1H), 1.93 (m, 1H), 0.13 (s, 9H) ; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 151.1, 143.8, 133.6, 131.4, 130.9, 129.6, 128.1, 127.3, 54.2, 52.7, 41.7, 29.0, 27.2, 21.5, -0.8 ; Anal. Calc'd for $C_{19}H_{27}NO_2SSi$: C, 63.11; H, 7.53; N, 3.87. Found: C, 62.92; H, 7.47; N, 3.91.

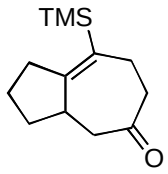


6r

Table 1, entry 18:

***N*-(4-Methylbenzenesulfonyl)-5-(trimethyl-silyl)-2,3,4,6,7,9a-hexahydro-1*H*-cyclohepta[c]pyridine** (**6r**): To a test tube containing $CpRu(CH_3CN)_3PF_6$ (4 mg, 0.009 mmol) was added a solution of vinylcyclopropane **5r** (18 mg, 0.048 mmol) in acetone (0.4 mL) and the resulting orange solution stirred at 50 ºC for 2 h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 6:1 petroleum ether:diethyl ether to afford **6r** (12 mg, 67%) as a clear film.

IR (film): 2955, 2923, 2852, 1599, 1346, 1248, 1161, 1093 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.33 (m, 1H), 5.18 (m, 1H), 4.82 (m, 1H), 3.89 (m, 1H), 3.09 (m, 3H), 2.43 (s, 3H), 2.16 (m, 1H), 2.05 (m, 2H), 0.09 (s, 9H) ; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 143.9, 139.3, 136.5, 135.2, 129.6, 128.5, 127.4, 127.2, 52.4, 46.4, 31.1, 30.7, 30.3, 25.3, 21.5, -1.7 ; HRMS (EI+) Calc'd for $C_{20}H_{29}NO_2SSi$ [M]$^+$: 375.1688. Found: 375.1689.

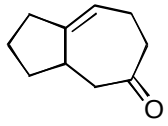


6s

Table 1, entry 19:

8-Trimethylsilanyl-2,3,3a,4,6,7-hexahydro-1H-azulen-5-one (**6s**): To a test-tube under Ar with $[CpRu(CH_3CN)_3]PF_6$ (9.6 mg, 0.022 mmol) was added a solution of **5s** (74.2 mg, 0.296 mmol) in 2.2 mL acetone. The reaction was stirred at room temperature for 10 h. The reaction mixture was concentrated *in vacuo* and the residue purified by flash chromatography (silica gel, 10:1 petroleum ether:diethyl ether) to yield **6s** (48.4 mg, 0.217 mmol, 73%) as a clear, light yellow oil.

R_f=0.68 (1:1 petroleum ether:ether); IR (film) 2955, 2851, 1707, 1430, 1319, 1284, 1260, 1204, 1138, 1073, 804 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.52-2.28 (m, 6H), 1.99 (m, 2H), 1.90 (dd, J=13.1, 10.3 Hz, 1H), 1.36-1.25 (m, 4H), 0.07 (s, 9H) ; ^{13}CNMR (75 MHZ, $CDCl_3$) δ 210.1, 145.2, 132.4, 41.9, 40.2, 39.8, 36.5, 36.4, 31.1, 21.2, 0.1 ; Anal. Calc'd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 70.45; H, 10.05.

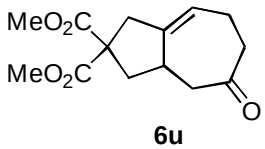


6t

Table 1, entry 20:

2,3,3a,4,6,7-Hexahydro-1H-azulen-5-one (**6t**): To a test-tube under Ar with $[CpRu(CH_3CH)_3]PF_6$ (21 mg, 0.048 mmol) was added a solution of **5t** (211 mg, 0.80 mmol) in 2.0 mL dry acetone via cannula. The reaction was stirred at room temperature for 5 h. The reaction mixture was concentrated *in vacuo*, and the residue was purified by flash chromatography (silica gel, 10:1 petroleum ether:diethyl ether) to yield 86.5 mg **6t** (86.5 mg, 0.58 mmol, 72%) as a clear, light yellow oil.

R_f=0.65 (1:1 petroleum ether:ether); IR (thin film) 2936, 2851, 1705, 1442, 1376, 1214, 1101, 1039 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.63 (m, 1H), 3.15-3.03 (m, 2H), 2.96 (dd, J= Hz, 1H), 2.62 (dd, J= Hz, 1H), 2.46 (dd, J= Hz, 1H), 2.40 (m, 1H), 2.29 (m, 1H), 2.09 (m, 4H), 1.56-1.42 (m, 2H) ; ^{13}CNMR (75 MHZ, $CDCl_3$) δ 207.6, 147.3, 119.5, 42.2, 40.4, 38.4, 36.3, 34.9, 33.6, 29.9, 20.0 ; Anal. Calc'd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.88; H, 9.53.



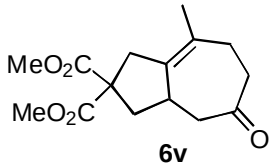
6u

Table 1, entry 21:

5-Oxo-3,3a,4,5,6,7-hexahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (**6u**):[8] To a test-tube with $[CpRu(CH_3CN)_3]PF_6$ (15.2 mg, 0.035 mmol) was added a solution of **5u** (99.6 mg,

[8] Wender, P.A.; Dyckman, A.J.; Husfeld, C.O.; Kadereit, D.; Love, J.A.; Rieck, H. *J. Am. Chem. Soc.* **1999**, *121*, 10442.

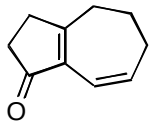
0.338 mmol) in 3.5 mL acetone. The reaction was stirred at room temperature for 2.5 h. The reaction mixture was concentrated *in vacuo* and the residue purified by flash chromatography (silica gel, 2:1 petroleum ether:diethyl ether) to yield unreacted **5u** (6.1 mg, 0.021mmol, 6%) and cycloadduct **6u** (70.2 mg, 0.264 mmol, 71%, 75% BRSM) as a clear, colorless oil.
R_f=0.23 (1:1 petroleum ether:ether); IR (film) 2954, 1734, 1708, 1435, 1285, 1260, 1205, 1168, 1074, 948, 885 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.66 (m, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.08-2.99 (m, 3H), 2.88 (m, 1H), 2.63 (m, 2H), 2.50 (dd, J=15.5, 12.2 Hz, 1H), 2.38 (m, 2H), 2.21 (m, 1H), 1.89 (dd, J=12.8, 10.4 Hz, 1H) ; ^{13}CNMR (125 MHZ, $CDCl_3$) δ 211.9, 171.8, 171.6, 143.1, 121.3, 58.5, 52.9, 52.8, 48.6, 42.0, 41.6, 41.2, 36.5, 25.3 ; HRMS (EI+) Calc'd for $C_{14}H_{18}O_5$ $[M]^+$: 266.1154. Found 266.1159.



6v

Table 1, entry 22:

8-Methyl-5-oxo-3,3a,4,5,6,7-hexahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester (6v):[8] To a test-tube with $[CpRu(CH_3CN)_3]PF_6$ (14.2 mg, 0.032 mmol) was added a solution of **5v** (102.1 mg, 0.331 mmol) in 3.2 mL acetone. The reaction was stirred at room temperature 1.8 h. The reaction mixture was concentrated *in vacuo* and the residue purified by flash chromatography (silica gel, 2:1 petroleum ether:diethyl ether) to yield cycloadduct **6v** (68.5 mg, 0.244 mmol, 74%) as a clear, colorless oil.
R_f=0.23 (1:1 petroleum ether:ether); IR (film) 2955, 2848, 1733, 1705, 1435, 1288, 1253, 1204, 1171, 1072, 1011, 886, 830 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.74 (s, 3H), 3.05 (d, J=16.0 Hz, 2H), 2.92 (m, 2H), 2.59 (m, 2H), 2.43 (dd, J=16.1, 11.8 Hz) 2.33 (m, 3H), 1.84 (dd, J=12.8, 11.1 Hz, 1H), 1.68 (s, 3H) ; ^{13}CNMR (125 MHZ, $CDCl_3$) δ 212.1, 172.0, 171.8, 135.4, 128.1, 58.4, 52.9, 52.8, 48.4, 41.6, 39.8, 37.0, 31.7, 21.7 ; HRMS (EI+) Calc'd for $C_{15}H_{20}O_5$ $[M]^+$: 280.1311. Found 280.1326.



6u

Table 1, entry 23:

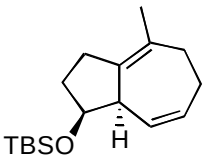
3,4,5,6-Tetrahydro-2*H*-azulen-1-one (6u):[9]

To a test tube containing $CpRu(CH_3CN)_3PF_6$ (11 mg, 0.026 mmol) was added a solution of vinylcyclopropane **5u** (50 mg, 0.260 mmol) in acetone (1.3 mL) and the resulting orange solution stirred at room temperature for 3h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 1:1 diethyl ether:petroleum ether to afford a 5:1 mixture of ketones **5u** and **5u'** (41 mg, 68%). The ratio of **5u**:**5u'** was determined by ^{1}H-NMR integration of one of the olefinic protons: for **5u** a doublet at 6.17 ppm (1H) and for **5u'** a doublet at 6.45 ppm (1H).

[9] Hiyama, T.; Shinoda, M.; Saimoto, H.; Nazaki, M. *Bull Chem. Soc. Jpn.* **1981**, *54*, 2747.

IR (film): 3022, 2922, 2850, 1697, 1628, 1418, 1275, 1184, 1084, 989, 847, 759, 737 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.17 (d, *J* = 11.5 Hz, 1H), 5.95 (dt, *J* = 11.5 and 5.3 Hz, 1H), 2.65 (t, *J* = 5.7 Hz, 2H), 2.55 (m, 2H), 2.41 (m, 4H), 1.90 (p, *J* = 5.7 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 208.2, 174.8, 135.8, 134.4, 118.0, 35.3, 34.5, 31.4, 31.3, 23.1. HRMS (EI+) Calc'd for $C_{10}H_{12}O$ $[M]^+$: 148.0888. Found: 148.0888.

Additional signals for **5u'**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.55 (dt, *J* = 11.1 and 5.3 Hz, 1H), 6.45 (d, *J* = 11.1 Hz, 1H), 2.80 (m, 2H), 2.75 (m, 2H), 2.51-2.44 (m, 4H), 1.80 (m, 2H).



6aa

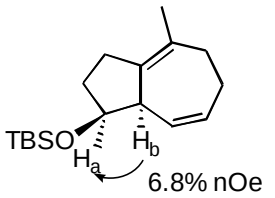
Table 2, entry 2:

3-(*tert*-Butyldimethylsilyloxy)-8-methyl-3,3a,6,7-hexahydroazulene (**6aa**): To a test tube containing $CpRu(CH_3CN)_3PF_6$ (2 mg, 0.005 mmol) was added a solution of vinylcyclopropane **5aa** (15 mg, 0.054 mmol) in DMF (0.5 mL) and the resulting orange solution stirred at room temperature for 6 h. The reaction mixture was directly chromatographed eluting with 3% diethyl ether: petroleum ether to afford a 5.1:1 mixture of **6aa** and its diastereomer (11 mg, 73%). The ratio of diastereomers was determined by ^{1}H-NMR integration of the bis-allylic protons: for the major diastereomer (**6aa**) a multiplet at 3.51 ppm (1H) and for minor diastereomer (**6aa**) a multiplet at 3.24 ppm (1H). Experiment done in acetone (entry 1 in **Table 2**) followed the same procedure.

IR (film): 2956, 2929, 2856, 1471, 1361, 1252, 1160, 1117, 1085, 1041, 835, 774 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.80 (ddt, *J* = 11.2, 2.6 and 1.7 Hz, 1H), 5.70 (m, 1H), 4.27 (dt, *J* = 5.7 and 4.0 Hz, 1H), 3.51 (m, 1H), 2.49 (m, 2H), 2.32-2.10 (m, 4H), 1.90 (m, 1H), 1.70 (m, 1H), 1.68 (s, 3H), 0.91 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 130.9, 129.3, 129.1, 127.7, 75.7, 46.5, 34.0, 32.4, 28.1, 26.1, 25.9, 21.1, 18.2, -4.5; HRMS (EI+) Calc'd for $C_{13}H_{22}OSi$ $[M - t\text{-Bu}]^+$: 222.1440. Found: 222.0863.

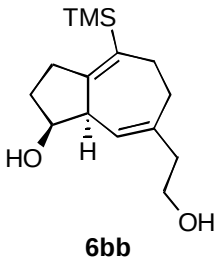
Additional signals for **6aa**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.63 (ddd, *J* = 11.2, 3.7 and 1.6 Hz, 1H), 3.84 (td, *J* = 8.7 and 5.7 Hz, 1H), 3.24 (m, 1H), 1.65 (s, 3H), 0.92 (s, 9H), 0.11 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 129.7, 129.9, 80.1, 50.3, 33.2, 32.6, 27.6, 26.4, 25.8, 20.4, 18.0, -4.3, -4.9.

nOe study:



δ_a=4.27 ppm
δ_b=3.51 ppm

6aa



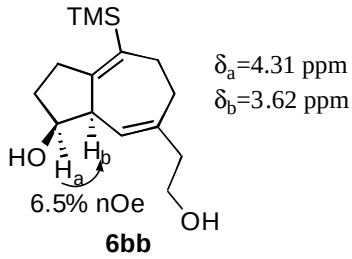
6bb

Table 2, entry 3:

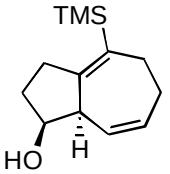
7-(2-Hydroxyethyl)-4-trimethylsilyl-1,2,3,5,6,8a-hexahydro-azulen-1-ol (6bb): To a solution of malonate **5bb** (20 mg, 0.075 mmol) in 2 mL of acetone under argon was added $CpRu(CH_3CN)_3PF_6$ (4 mg, 0.08 mmol). The mixture was stirred at rt for 3 h. Without workup, the mixture was chromatographed (5% to 95% of diethyl ether in petroleum ether) to afford cycloadduct **6bb** (15 mg, 0.56 mmol, 75%, d.r.=5:1) as a colorless oil.

IR (neat): 3356w, 2925s, 2854s, 1628w, 1456w, 1247m, 1156w, 1065w, 936w, 904w, 853m, 834m, 754w, 686w cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.44 (s, 1H), 4.31 (bs, 1H), 3.67 (m, 2H), 3.62 (m, 1H), 2.60 (m, 1H), 2.42 (m, 2H), 2.23 (m, 3H), 2.04 (m, 2H), 1.83 (m, 2H), 1.70 (m, 1H), 0.14 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.3, 139.4, 133.3, 122.8, 75.4, 60.0, 49.6, 43.6, 33.4, 31.0, 29.7, 29.4, -0.34. MS Calc'd for $C_{15}H_{26}O_2Si$ [M^+]: 266. Found: 266.

nOe study:



6bb



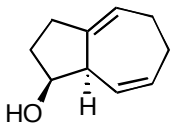
6cc

Table 2, entry 4:

4-Trimethylsilanyl-1,2,3,5,6,8a-hexahydro-azulen-1-ol (6cc):

To a test tube containing $CpRu(CH_3CN)_3PF_6$ (110 mg, 0.252 mmol) was added a solution of vinylcyclopropane **5cc** (553 mg, 2.49 mmol) in acetone (10 mL) and the resulting orange solution stirred at room temperature for 30 minutes. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 4:1 petroleum ether: diethyl ether to afford **6cc** (418 mg, 75%) as a colorless liquid.

IR(film): 3361, 2954, 1626, 1430, 1247, 1067, 848 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.80 (m, 1H), 5.53 (d, *J* = 11.5 Hz, 1H), 4.29 (s, 1H), 3.69 (br.s, 1H), 2.70-2.56 (m, 1H), 2.49 (d, *J* = 12.7 Hz, 1H), 2.39 (dd, *J* = 15.9 and 7.6 Hz, 1H), 2.27-2.15 (m, 2H), 2.06 (m, 1H), 1.86 (ddt, J = 12.7, 7.6 and 2.2 Hz, 1H), 1.67-1.55 (m, 2H), 0.12 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 156.2, 133.6, 133.1, 124.7, 75.1, 50.0, 33.5, 31.0, 29.6, 28.2, –0.3.



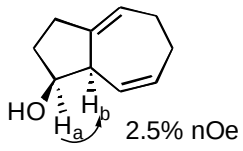
6dd

Table 2, entry 5:

1,2,3,5,6,8a-Hexahydro-azulen-1-ol (6dd): To a solution of malonate **5dd** (150 mg, 1.0 mmol) in 3 mL of acetone under argon was added $CpRu(CH_3CN)_3PF_6$ (43 mg, 0.10 mmol). The mixture was stirred at rt for 4 h. Without workup, the mixture was chromatographed (5% to 30% of diethyl ether in petroleum ether) to afford cycloadduct **6dd** (129 mg, 0.86 mmol, 88%, d.r.>10:1) as a colorless oil.

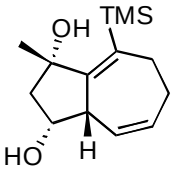
IR (neat): 3386b, 2932s, 2901s, 1447m, 1433m, 1328w, 1173m, 1155m, 1080m, 1069m, 1016w, 982w, 935w, 895w, 846s, 793w, 731w cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.97 (m, 1H), 5.77 (t, *J*=2.0 Hz, 1H), 5.68 (dt, *J*=1.0, 11.5 Hz, 1H), 4.30 (s, 1H), 3.52 (s, 1H), 2.60 (m, 1H), 2.35 (m, 3H), 2.10 (m, 2H), 1.82 (m, 1H), 1.71 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 143.1, 133.4, 126.7, 123.3, 76.0, 49.1, 32.7, 30.3, 27.1, 26.1. MS Calc'd for $C_9H_{14}O$ [M^+]: 150. Found: 150.

nOe study:



δ_a=4.30 ppm
δ_b=3.52 ppm

6dd

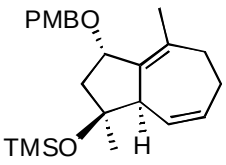


6ee

Table 2, entry 6:

1-Methyl-8-(trimethylsilyl)-1,2,3,3a,6,7-hexahydroazulene-1,3-diol (6ee): To a solution of **5ee** (600 mg, 2.38 mmol) in dichloromethane (12 mL) was added $CpRu(CH_3CN)_3PF_6$ (5 mol%, 52 mg, 0.118 mmol) at -78°C. The solution was warmed to 15°C over 2.5 h. Without workup, the reaction mixture was chromatographed with 50% of diethylether in petroleum ether to give **6ee** (485 mg, 1.92 mmol, 81 % yield) as a white solid.

Mp.: 137 ^{o}C. IR (neat): 3277brm, 2919w, 1390w, 1246w, 1072w, 920w, 838w cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.72-5.60 (m, 1H), 5.55-5.50 (m, 1H), 4.11 (s, br, 1H), 3.77 (s, br, 1H), 2.60-2.30 (m, 3H), 2.30-2.10 (m, 2H), 2.06-1.88 (m, 1H), 1.97 (dd, *J*=13.6, 2.8 Hz, 1H), 1.72 (dd, *J*=13.6, 4.0 Hz, 1H), 1.39 (s, 3H), 0.16 (s, 9H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ:162.7, 138.4, 132.2, 125.8, 79.6, 74.1, 51.0, 49.5, 31.8, 28.5, 27.6, 1.3; Anal. Calc'd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58. Found: C, 66.70; H, 9.44. See supplementary file for X-ray data.



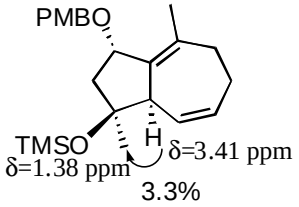
6ff

Table 2, entry 7:

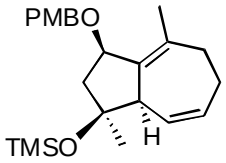
(1*S, 3*R**, 10*R**)-[3-(4-Methoxybenzyloxy)-1,4-dimethyl-1,2,3,5,6,8a-hexahydro-azulen-1-yloxy]-trimethylsilane** (**6ff**): To vinylcyclopropane **5ff** (95 mg, 0.25 mmol) in 1 mL of distilled acetone was added $CpRu(CH_3CN)_3PF_6$ (5.5 mg, 0.0125 mmol) at rt. The solution was stirred for 1.5 h. After removal of the solvent, the residue was separated by flash chromatography eluting with 5% to 20% diethyl ether in petroleum ether to afford **6ff** (63 mg, 0.16 mmol, 65%).

IR (film) cm^{-1}: 2958s, 2829s, 2853m, 1612w, 1514s, 1443w, 1375w, 1302w, 1240s, 1173m, 1143m, 1107s, 1076ss, 1034s, 915w, 840s; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.27 (d, J=8.7 Hz, 2H), 6.86 (d, J=8.4 Hz, 2H), 5.76 (s, 2H), 4.56 (t, J=6.9 Hz, 1H), 4.44 (d, J=10.5 Hz, 1H), 4.37 (d, J=10.5 Hz, 1H), 3.79 (d, J=1.2 Hz, 3H), 3.41 (bs, 1H), 2.37 (m, 2H), 2.24 (dd, J=7.2, 12.9 Hz, 1H), 2.02 (m, 2H), 1.73 (s, 3H), 1.68 (m, 1H), 1.38 (s, 3H), 0.10 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.1, 137.5, 135.0, 130.7, 130.2, 129.8, 128.7, 113.7, 80.5, 78.1, 70.3, 55.3, 52.3, 45.80, 33.2, 27.2, 25.4, 21.5, 2.40. HRMS Calc'd for $C_{23}H_{34}O_3Si$ (M-CH_3^+): 386.2277. Found: 386.2260;

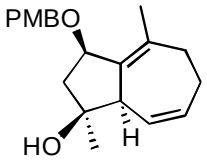
nOe:



observed nOe in major diastereomer of **6ff**



6gg



6gg'

Table 2, entry 8:

(1*R,3*R**,10*R**)-[3-(4-Methoxy-benzyloxy)-1-4-dimethyl-1,2,3,5,6,8a-hexahydro-azulen-1-yloxy]-trimethylsilyl ether** (**6gg**) **and (1*R**, 3*R**, 10*R**)-3-(4-methoxy-benzyloxy)-1-4-dimethyl-1,2,3,5,6,8a-hexahydroazulen-1-ol** (**6gg'**): To cyclopropane **5gg** (0.44 g, 1.14 mmol) in 2 mL of distilled acetone was added $CpRu(CH_3CN)_3PF_6$ (25 mg, 0.057 mmol) at rt. The solution was stirred for 1.5 h. After removal of the solvent, the residue was separated by flash chromatography eluting with 5% to 20% diethyl ether in petroleum ether to afford **6gg** (140 mg, 0.45 mmol, 39%) and **6gg'** (144 mg, 0.37 mmol, 33%).

For **6gg**: IR (film): 2960m, 2930m, 1613m, 1514s, 1442m, 1375m, 1302m, 1249s, 1173s, 1150m, 1108s, 1074m, 1036s, 889, 840s, 764m cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.27 (d, J=8.5 Hz, 2H), 6.90 (d, J=8.5 Hz, 2H), 5.89 (m, 1H), 5.63 (m, 1H), 4.53 (d, J=11.5 Hz, 1H), 4.41 (m, 1H), 4.35 (d, J=11.5 Hz, 1H), 3.82 (s, 3H), 3.55 (m, 1H), 3.31 (s, 1H), 2.58 (m, 1H), 2.40-2.15 (m, 4H), 1.98 (m, 1H), 1.84 (s, 3H), 1.46 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 158.9, 139.4, 135.3, 131.0, 129.0, 128.7, 128.6, 122.3, 78.0, 69.9, 55.2, 54.3, 52.1, 44.5, 32.9, 28.9, 25.9, 20.7; HRMS (EI+) Calc'd for $C_{22}H_{31}O_3Si$ [M - CH_3]$^+$: 371.2042. Found: 371.2041.

For **6gg'**: IR (film): 3496b, 2959m, 2929m, 1613m, 1586w, 1514s, 1438w, 1303w, 1249s, 1174m, 1116m, 1089m, 1034s, 923w, 825m cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.27 (d, J=8.5

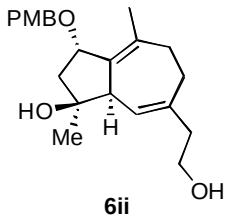
Hz, 2H), 6.88 (d, J=8.5 Hz, 2H), 5.86 (dd, J=1.5, 11.0 Hz, 1H), 5.82 (m, 1H), 4.53 (d, J=11.0 Hz, 1H), 4.46 (d, J=4.5 Hz, 1H), 4.40 (d, J=11.0 Hz, 1H), 3.82 (d, J=0.5 Hz, 3H), 3.55 (s, 1H), 3.34 (d, J=2.0 Hz, 1H), 2.52 (m, 1H), 2.32 (m, 1H), 2.20 (m, 2H), 2.00 (dd, J=6.0, 13.0 Hz, 1H), 1.75 (d, J=2.0 Hz, 3H), 1.59 (dd, J=4.5, 14.5 Hz, 1H), 1.34 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.2, 138.4, 138.1, 129.9, 129.8, 128.1, 113.7, 94.1, 79.2, 78.6, 69.8, 55.2, 51.5, 43.0, 32.8, 25.9, 24.7, 21.4; HRMS Calc'd for $C_{20}H_{26}O_3$: 314.1882. Found: 314.1880.

TBDPSO PMBO **6hh**

Table 2, entry 9:

1-(*tert*-Butyldiphenylsilyloxy)-3,8-dimethylsilyloxy-1,2,3,3a,6,7-hexahydroazulene (**6hh**): To cyclopropane **5hh** (504 mg, 1 mmol) in 4 mL of distilled acetone was added $CpRu(CH_3CN)_3PF_6$ (43 mg, 0.1 mmol) at rt. The solution was stirred for 2 h. The mixture was directly purified by flash chromatography eluting with 5% diethyl ether in petroleum ether to afford **6hh** (328 mg, 0.65 mmol, 65%) as a brown oil.

IR (film): 3071, 2960, 2858, 1473, 1428, 1251, 1184, 1111, 1083, 840, 702 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.79-7.74 (m, 4H), 7.45-7.36 (m, 6H), 5.88 (ddt, *J*=11.5, 2.7, 2.1 Hz, 1H), 5.58 (dddd, *J*=11.5, 3.7, 3.4, 3.4 Hz, 1H), 4.77 (t, *J*=6.8 Hz, 1H), 3.31 (brs, 1H), 2.81 (ddd, *J*=13.4, 10.0, 6.8 Hz, 1H), 2.23 (m, 2H), 1.89 (dd, *J*=12.0, 7.1 Hz, 1H), 1.81 (dt, *J*=13.4, 4.0 Hz, 1H), 1.74 (s, 3H), 1.54 (dddd, *J*=12.0, 6.6, 1.2 Hz, 1H), 1.12 (s, 3H), 1.04 (s, 9H), -0.01 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 142.3, 136.0, 135.9, 134.8, 134.0, 129.4, 129.3, 128.5, 128.2, 127.4, 127.3, 78.3, 73.0, 51.5, 49.5, 33.4, 29.8, 27.0, 19.5, 2.2; Anal. Calc'd for $C_{31}H_{44}O_2Si_2$: C, 73.75; H, 8.78. Found: C, 73.70; H, 8.72.



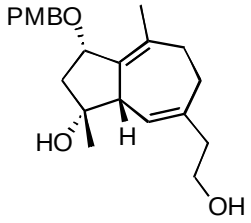
6ii

Table 2, entry 10:

(1*S,3*S**,9*R**)-7-(2-Hydroxyethyl)-3-(4-methoxybenzyloxy)-1,4-dimethyl-1,2,3,5,6,8a-hexahydro-azul-en-1-ol** (**6ii**): To enyne **5ii** (220 mg, 0.512 mmol) in 3 mL of distilled acetone under argon at rt was added $CpRu(CH_3CN)_3PF_6$ (22 mg, 0.051 mmol). It was stirred for 2 h and chromatographed eluting with 5% diethyl ether in petroleum ether to 100% diethyl ether to afford the cycloadduct **6ii** (183 mg, 0.461mmol, 90 %) as a single diastereomer.

IR (film): 3407b, 2958s, 2926s, 2856m, 1728s, 1613w, 1514m, 1464m, 1378w, 1282m, 1249s, 1121m, 1073m, 1037m, 861w, 821w, 773w, 741w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.29 (d, J=9.0 Hz, 2H), 6.88 (d, J=9.0 Hz, 2H), 5.52 (s, 1H), 4.46 (t, J=7.0 Hz, 1H), 4.46 (d, J=11.0 Hz, 1H), 4.39 (d, J=11.0 Hz, 1H), 3.82 (s, 3H), 3.86 (m, 2H), 3.50 (m, 1H), 2.47 (t, J=11.5 Hz, 1H), 2.35 (m, 4H), 2.08 (m, 2H), 1.78 (d, J=2.0 Hz, 3H), 1.72 (dd, J=8.0, 13.0 Hz, 1H), 1.46 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.2, 141.1, 136.9, 130.4, 129.8, 125.5, 124.3, 113.7, 78.5,

70.4, 60.1, 55.3, 51.1, 45.8, 42.6, 33.1, 30.3, 29.5, 25.7, 22.0; HRMS (EI+) Calc'd for $C_{22}H_{30}O_4$ $[M]^+$: 358.2144. Found: 358.2143.



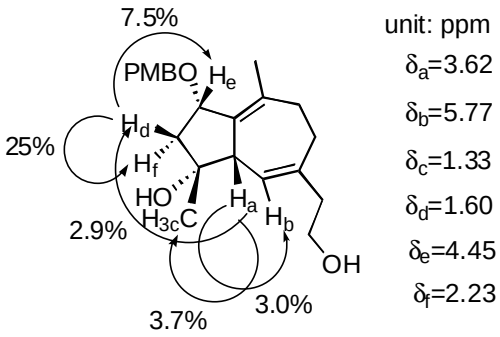
6jj

Table 2, entry 11:

(1*R,3*S**,9*S**)-7-(2-Hydroxy-ethyl)-3-(4-methoxybenzyloxy)-1,4-dimethyl-1,2,3,5,6,8a-hexahydro-azul-en-1-ol** (**6jj**): To substrate **5jj** (140 mg, 0.33 mmol) in 2.5 mL of acetone was added $CpRu(CH_3CN)_3PF_6$ (7 mg, 0.016 mmol) at rt. The reaction mixture was stirred for 5 h and chromatographed eluting with 5% to 50% ethyl acetate in petroleum ether to afford cycloadduct **6jj** as a single diastereomer (81 mg, 0.23 mmol, 70%).

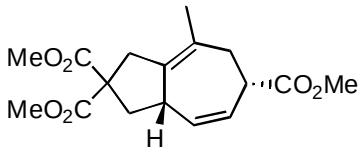
IR (film): 3430b, 2929s, 1612m, 1514s, 1440m, 1372m, 1304m, 1250s, 1175m, 1096m, 1034s, 924w, 846m, 824m cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.15 (d, *J*=9.0 Hz, 2H), 6.76 (d, *J*=8.4 Hz, 2H), 5.63 (s, 1H), 4.43 (d, *J*=10.8 Hz, 1H), 4.33 (d, *J*=4.8 Hz, 1H), 4.24 (d, *J*=10.8 Hz, 1H), 3.69 (s, 3H), 3.53 (t, *J*=6.0 Hz, 2H), 3.14 (bs, 1H), 2.35 (s, 1H), 2.17 (m, 6H), 1.94 (m, 4H), 1.54 (d, *J*=2.1 Hz, 3H), 1.46 (dd, *J*=4.8, 14.1 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.2, 137.6, 137.4, 137.0, 129.9, 129.5, 125.7, 113.6, 79.9, 79.3, 70.0, 59.9, 55.0, 51.0, 42.4, 42.0, 32.1, 29.5, 24.5, 21.3; HRMS (EI+) Calc'd for $C_{22}H_{28}O_3$ $[M - H_2O]^+$: 340.2038. Found: 340.2036.

nOe:

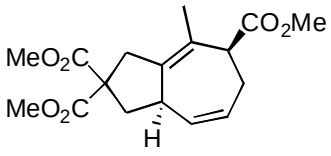


6jj

Table 3



15a



16a

***Trans*-8-methyl-3,5,6,8a-tetrahydro-1*H*-azulene-2,2,6-tricarboxylic acid trimethyl ester** (**15a**) **and *Trans*-4-methyl-3,5,6,8a-tetrahydro-1*H*-azulene-2,2,5-tricarboxylic acid trimethyl ester** (**16a**):[10]

Entry 1

Ester **14a** (40 mg, 0.12 mmol) in 0.6 ml of distilled acetone was degassed by argon before the addition of $CpRu(CH_3CN)_3PF_6$ (6 mg, 0.012 mmol). The resulting red solution was stirred at rt for 1 h. Without workup of the reaction mixture, flash chromatography eluting with 5 %-10 % diethyl ether in petroleum ether afforded yellow oil as a mixture of **15a** and **16a** (36 mg, 0.11 mmol, 90 %). The ratio of **15a** to **16a** is 1:2. The stereochemistry of these two compounds has been confirmed by comparison with known compound.[10]

Entry 2

Ester **14a** (15 mg, 0.047 mmol) in 0.3 ml of DMF was degassed by argon before the addition of $CpRu(CH_3CN)_3PF_6$ (3 mg, 0.007 mmol). The resulting black solution was stirred at rt for 1 h. Without workup, flash chromatography eluting with 5%-15% diethyl ether in petroleum ether afforded a yellow oil as a mixture of **15a** and **16a** (12 mg, 0.038 mmol, 80 %). The ratio of **15a** to **16a** is 1:2.5. The stereochemistry of these two compounds has been confirmed by comparison with known compound.[10]

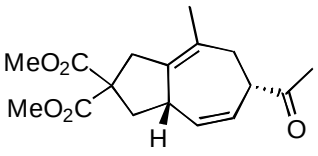
Entry 3:

To a solution of **14a** (5 mg, 0.016 mmol) in 0.4 mL of acetone was added In(OTf) (0.9 mg, 0.0016 mmol) and **4** (0.7 mg, 0.0016 mmol) under argon at rt. The mixture was stirred for 2h and purified by flash chromatography eluting with 5% diethyl ether in petroleum ether without workup, to afford a 2.3:1 mixture of **15a** and **16a** (4 mg, 0.013 mmol, 80%).

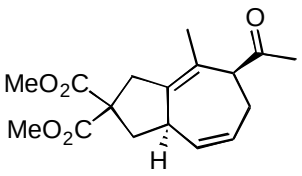
Entry 4

Ester **14a** (9 mg, 0.028 mmol) in 0.2 ml of distilled acetone was degassed by argon before the addition of hexamethylphosphonamide (0.50 mg, 0.003 mmol, 0.50 ul) and $CpRu(CH_3CN)_3PF_6$ (1.2 mg, 0.003 mmol) in sequence. The resulting black solution was stirred at rt for 2 hrs. Flash chromatography eluting with 5 %-15 % diethyl ether in petroleum ether afforded yellow oil as a mixture of **15a** and **16a** (7 mg, 0.022 mmol, 78 %). The ratio of **15a** to **16a** is 1:2. The stereochemistry of these two compounds has been confirmed by comparison with known compound.[10]

Major isomer **16a**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.56-5.60 (m, 1H), 5.48 (dq, J=1, 1.8, 11.0 Hz, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.70 (s, 3H), 3.62-3.66 (m, 1H), 3.60 (d, J=9.7 Hz, 1H), 3.02 (d, J=16.8 Hz, 1H), 2.95 (d, J=16.8 Hz, 1H), 2.70 (ddd, J=1.5, 8.4, 12.8 Hz, 1H), 2.47 (dm, J=15.8 Hz, 1H), 2.34-2.41 (m, 1H), 2.02 (dd, J=10.8, 12.8 Hz, 1H), 2.02 (t, J=12.4 , 1H Hz), 1.61 (d, J=1.5 Hz, 3H); Minor isomer **15a**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.83 (ddd, J=2.9, 6.1, 10.7 Hz, 1H), 5.68 (ddd, J=2.0, 2.7, 10.7 Hz, 1H), 3.73 (s, 6H), 3.70 (s, 3H), 3.53-3.60 (m, 2H), 3.02 (d, J=16.8 Hz, 1H), 2.85 (d, J=16.8 Hz, 1H), 2.68 (ddd, J=2.0, 7.9, 12.6 Hz, 1H), 2.57 (d, J=16.1 Hz, 1H), 2.27 (dd, J=10.1, 15.6 Hz, 1H), 2.02 (t, J=12.4 Hz, 1H), 1.65 (s, 3H).



15b

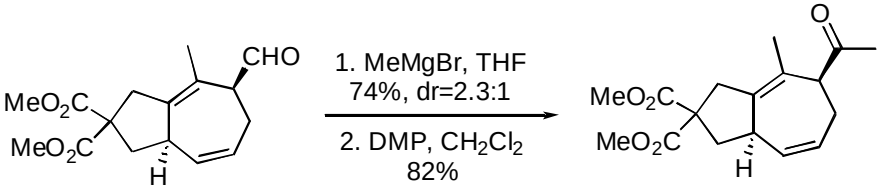


16b

***Trans*-6-acetyl-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (15b) and *Trans*-7-acetyl-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (16b)**: Table 3, entry 5: To a solution of 14b (18 mg, 0.059 mmol) in 0.5 mL of acetone was added 4 (2.6 mg, 0.0059 mmol) under argon at rt. The mixture was stirred

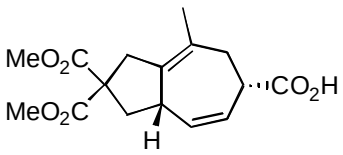
for 3h and purified by flash chromatography eluting with 5%-50% diethyl ether in petroleum ether without workup, to afford a 2:1 mixture of 15b and 16b (15 mg, 0.049 mmol, 83%).
Entry 6: To a solution of **14b** (16 mg, 0.052 mmol) in 0.5 mL of acetone was added In(OTf) (4.4 mg, 0.0078 mmol) and **4** (3.4 mg, 0.0078 mmol) under argon at rt. The mixture was stirred for 7h and purified by flash chromatography eluting with 5%-50% diethyl ether in petroleum ether without workup, to afford a 1:1.2 mixture of **15b** and **16b** (14 mg, 0.046 mmol, 88%).
IR (film): 2955w, 2918w, 2851w, 1735s, 1715s, 1435m, 1357w, 1273s, 1236m, 1202m, 1165m, 1076w, 952w, 885w, 744w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) of major isomer **15b**: δ 5.82 (ddd, J=2.5, 6.0, 10.5 Hz, 1H), 5.74 (ddd, J=1.5, 2.5, 10.5 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.70 (m, 2H), 3.04 (d, J=16.5 Hz, 1H), 2.87 (dt, J=2.0, 17.0 Hz, 1H), 2.71 (dq, J=2.5, 10.0 Hz, 1H), 2.57 (m, 1H), 2.29 (m, 1H), 2.19 (s, 3H), 2.07 (q, J=10.5 Hz, 1H), 1.66 (d, J=2.0 Hz, 3H); ^{1}H-NMR (500 MHz, $CDCl_3$) of minor isomer **16b**: δ 5.62 (m, 1H), 5.57 (d, J=10.5 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.70 (m, 1 H), 3.54 (d, J=8.0 Hz, 1H), 3.05 (d, J=17.0 Hz, 1H), 2.97 (d, J=17.0 Hz, 1H), 2.72 (ddd, J=1.5, 8.0, 10.5 Hz, 1H), 2.55 (dm, J=13.5 Hz, 1 H), 2.31 (m, 1H), 2.16 (s, 3H), 2.08 (dd, J=10.5 Hz, 13.0 Hz, 1H), 1.59 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) of major isomer **15b**: δ 209.3, 172.0, 171.8, 134.6, 134.3, 127.6, 126.8, 58.1, 52.9, 52.8, 50.5, 41.2, 40.0, 39.4, 34.1, 29.6, 28.9; ^{13}C-NMR (125 MHz, $CDCl_3$) of minor isomer **16b**: δ 210.4, 172.1, 171.9, 138.3, 133.3, 127.7, 126.1, 58.3, 55.2, 52.9, 52.8, 41.3, 40.1, 39.4, 30.1, 29.7, 27.6; HRMS (EI+) Calc'd for $C_{17}H_{22}O_5$ $[M]^+$: 306.1467. Found: 306.1457.

Procedure for Verification of Stereochemistry of **16b**:
***Trans*-7-acetyl-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (16b)**:

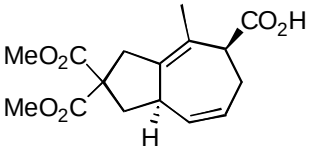


16l **16b**

At -78 °C to a solution of **16l** (20 mg, 0.068 mmol) in 0.5 mL of THF was added methyl magnesium bromide (46 uL, 3 M in THF, 0.14 mmol). The mixture was slowly warmed to rt over 3h. Directly purification by flash chromatography (5%-50% diethyl ether in petroleum ether) without further workup gave a mixture of two diastereomeric alcohols (16 mg, 0.052 mmol). To this mixture was added 0.5 mL of dichloromethane, sodium bicarbonate (7 mg, 0.08 mmol) and DMP (26 mg, 0.062 mmol). It was stirred at rt for 8 h and chromatographed eluting with 5% diethyl ether in petroleum ether to afford ketone **16b** (13 mg, 0.042 mmol, 82%).
IR (film): 2955w, 2918w, 2851w, 1735s, 1715s, 1435m, 1357w, 1273s, 1236m, 1202m, 1165m, 1076w, 952w, 885w, 744w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.62 (m, 1 H), 5.57 (d, J=10.5 Hz, 1 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 3.70 (m, 1 H), 3.54 (d, J=8.0 Hz, 1 H), 3.05 (d, J=17.0 Hz, 1 H), 2.97 (d, J=17.0 Hz, 1 H), 2.72 (ddd, J=1.5, 8.0, 10.5 Hz, 1 H), 2.55 (dm, J=13.5 Hz, 1 H), 2.31 (m, 1 H), 2.16 (s, 3 H), 2.08 (dd, J=10.5 Hz, 13.0 Hz, 1 H), 1.59 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 210.4, 172.1, 171.9, 138.3, 133.3, 127.7, 126.1, 58.3, 55.2, 52.9, 52.8, 41.3, 40.1, 39.4, 30.1, 29.7, 27.6; HRMS (EI+) Calc'd for $C_{17}H_{22}O_5$ $[M]^+$: 306.1467. Found: 306.1457.



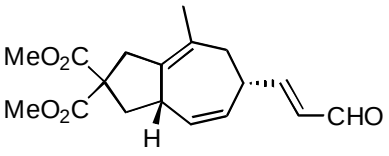
15c



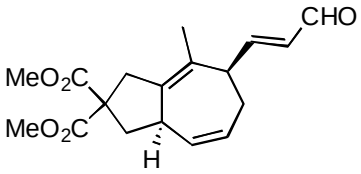
16c

Table 3, entry 7:

***Trans*-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2,6-tricarboxylic acid dimethyl ester (15c) and *Trans*-4-methyl-3,5,6,8a-tetrahydro-1*H*-azulene-2,2,6-tricarboxylic acid dimethyl ester (16c)**: Acid **14c** (20 mg, 0.065 mmol) in 0.35 ml of distilled acetone was degassed with argon before the addition of the $CpRu(CH_3CN)_3PF_6$ (4 mg, 0.01 mmol). The resulting dark brown solution was stirred at rt for 2 h. Flash chromatography eluting with 50 % ethyl acetate in petroleum ether afforded yellow oil as a mixture of **15c** and **16c** (15.6 mg, 0.051 mmol, 78 %). The ratio of **15c** to **16c** is 1:3. The stereochemistry of these two compounds has been confirmed by comparison with known compounds made in Wender's group.[1e] Both compounds were converted to methyl esters. The comparison with esters **15a** and **16a** established the stereochemistry of **15c** and **16c**.



15d



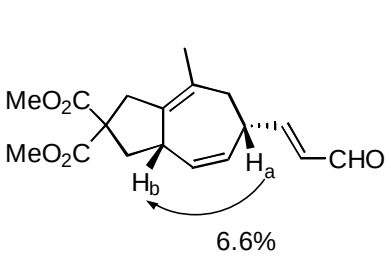
16d

Table 3, entry 9:

***Trans*-8-methyl-6-(3-oxo-propenyl)-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic ac-id dimethyl ester (15d) and *Trans*-8-methyl-7-(3-oxo-propenyl)-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (16d)**: Enal **14d** (22 mg, 0.069 mmol) in 0.5 ml of distilled acetone was degassed by argon before the addition of $CpRu(CH_3CN)_3PF_6$ (3 mg, 0.007 mmol). The resulting yellow solution was stirred at rt for 0.5 h. Flash chromatography eluting with 50 % diethyl ether in petroleum ether afforded a colorless oil as a mixture of **15d** and **16d** (18 mg, 0.057 mmol, 82 %). The ratio of **15d** to **16d** is 1:1.6. The stereochemistry of these two compounds was confirmed by nOe study.

IR (film): 2949m, 2924m, 2850m, 1732s, 1688s, 1628s, 1434s, 1257m, 1198m, 1162m, 1126m, 1072s, 979s cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) for major isomer **16d**: δ 9.50 (d, J=8.0 Hz, 1H), 6.79 (dd, J=7.5, 15.0 Hz, 1H), 6.05 (dd , J=8.0, 15.5Hz, 1H), 5.64 (m, 2H), 3.722 (s, 3H), 3.719 (s, 3H), 3.60 (m, 1H), 3.37 (m, 1H), 3.04 (d, J=17.0 Hz, 1H), 2.87 (m, 1H), 2.66 (m, 2H), 2.17 (m, 1H), 2.25 (m, 1H), 1.56 (s, 3H); ^{1}H-NMR (500 MHz, $CDCl_3$) for minor isomer **15d**: δ 9.51 (d, J=8.0 Hz, 1H), 6.78 (dd, J=7.0, 15.5 Hz, 1H), 6.10 (dd, J=7.5, 17.0 Hz, 1H), 5.63 (m, 1H), 5.45 (m, 1H), 3.74 (s, 3 H), 3.72 (s, 3H), 3.60 (m, 1H), 3.26 (m, 1H), 2.97 (d, J=16.5 Hz, 1H), 2.85 (m, 1H), 2.75 (m, J=14.0 Hz, 1H), 2.66 (m, 1H), 1.95 (m, 2H), 1.55 (s, 3H); δ ^{13}C-NMR (75 MHz, $CDCl_3$) for major isomer **16d**: δ 194.1, 171.0, 160.0, 136.5, 134.5, 132.9, 128.8, 127.8, 125.5, 58.0, 52.8, 45.1, 41.2, 40.0, 39.8, 37.1, 30.4, 19.8; ^{13}C-NMR (75 MHz, $CDCl_3$) for minor isomer **15d**: δ 194.0, 172.1, 159.8, 136.5, 133.4, 132.5, 127.2, 126.6, 52.3, 45.1, 41.6, 40.2, 39.8, 39.1, 29.7, 22.6; Anal. Calc'd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 67.70; H, 6.74.

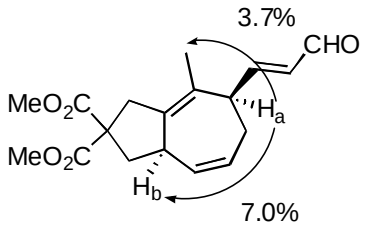
nOe study:



15d

δ_a= 3.60 ppm

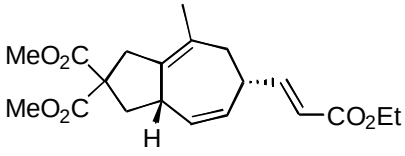
δ_a= 3.20 ppm



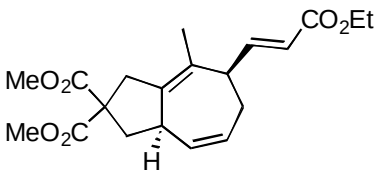
16d

δ_a= 3.60 ppm

δ_a= 3.37 ppm



15e



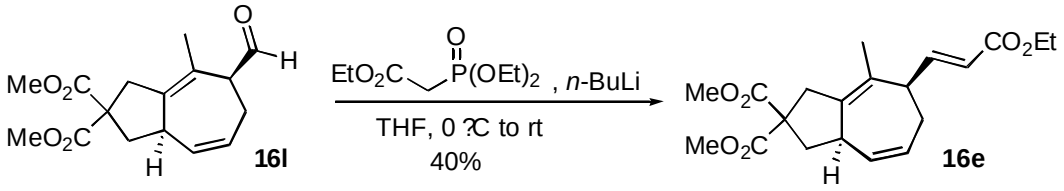
16e

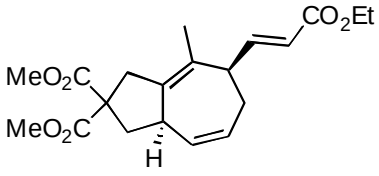
Table 3, entry 10:

***Trans*-6-(2-ethoxycarbonyl-vinyl)-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (15e) and *Trans*-7-(2-ethoxycarbonyl-vinyl)-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (16e)**: Ester **14e** (37 mg, 0.10 mmol) in 0.5 ml of DMF was degassed with argon. To this solution was added $CpRu(CH_3CN)_3PF_6$ (5 mg, 0.01 mmol). The solution was stirred at rt under argon for 2 h. Without further work-up, flash chromatography eluting with 10 %-25 % diethyl ether in petroleum ether afforded a light yellow oil as a mixture of **15e** and **16e** (32.5 mg, 0.089 mmol, 87 %). The ratio of **15e** to **16e** is 1:2.5.

IR (film) for mixture of **15e** and **16e**: 2956s, 2926s, 2855m, 1733s, 1710s, 1646s, 1436m, 1368m, 1258s, 1162s, 1047m, 983w, 862w, 822w, 767w cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) for major isomer **16e**: δ 6.93 (dd, J=8.7, 15.9 Hz, 1H), 5.75 (d, J=15.6 Hz, 1H), 5.62 (m, 2 H), 4.18 (q, J=7.2 Hz, 2 H), 3.75 (s, 3H), 3.74 (s, 3H), 3.61 (m, 1H), 3.18 (m, 1H), 3.12 (d, J=16.8 Hz, 1H), 2.87 (d, J=17.4 Hz, 1H), 2.65 (m, 2H), 2.17 (m, 1H), 2.04 (m, 1H), 1.56 (s, 3H), 1.30 (t, J=7.2 Hz, 3H); ^{1}H-NMR (300 MHz, $CDCl_3$) for minor isomer **15e**: δ 6.93 (dd, J=8.7, 15.9 Hz, 1H), 5.78 (d, J=15.9 Hz, 1H), 5.60 (m, 1H), 5.46 (m, 1H), 4.18 (q, J=7.2 Hz, 2 H), 3.75 (s, 3H), 3.73 (s, 3H), 3.51 (m, 1H), 2.98 (d, J=13.5 Hz, 1H), 2.70 (d, J=12.9 Hz, 1H), 2.60 (m, 3H), 2.06 (m, 2 H), 1.60 (s, 3H), 1.21 (t, J=7.2 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) major isomer **16e**: δ 167.3, 167.2, 161.9, 145.7, 131.2, 129.2, 123.4, 122.2, 116.7, 62.1, 55.5, 53.6, 48.0, 36.8, 35.1, 34.8, 34.3, 25.8, 24.9, 16.2; ^{13}C-NMR (75 MHz, $CDCl_3$) minor isomer **15e**: δ 167.3, 167.1, 162.0, 146.3, 131.1, 128.3, 124.9, 123.3, 116.4, 59.5, 55.4, 53.3, 40.0, 36.5, 35.1, 34.9, 32.5, 24.9, 20.1, 17.7; HRMS (EI+) Calc'd $C_{20}H_{26}O_6$ $[M]^+$: 362.1729. Found: 362.1724.

Procedure for verification of stereochemistry of **16e:**

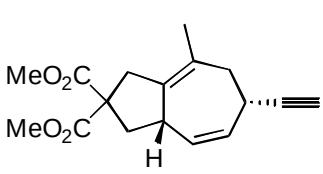




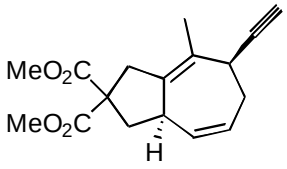
16e

***Trans*-7-(2-ethoxycarbonyl-vinyl)-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester** (**16e**): To triethylphosphonoacetate (27 mg, 0.12 mmol) in 0.4 mL of THF was added *n*BuLi (0.075 mL, 0.12 mmol, 1.6 M in hexane) at 0 °C. It was stirred at 0 °C for 15 min. before the addition of a 0.4 mL THF solution of aldehyde **16l** (33 mg, 0.11 mmol). The solution was warmed to rt and stirred for additional 1 h. The mixture was diluted with diethyl ether (10 mL), washed with water (2 mL), dried with magnesium sulfate and concentrated *in vacuo.* The residue was columned eluting with 5% to 10% diethyl ether in petroleum ether to afford ester **16e** (16 mg, 0.044 mmol, 40%).

IR (film): 2956m, 1732s, 1651w, 1435m, 1260s, 1198m, 1174s, 1074w, 1043w, 990w, 865w, 821w cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.93 (dd, J=8.7, 15.9 Hz, 1H), 5.75 (d, J=15.6 Hz, 1H), 5.62 (m, 2 H), 4.18 (q, J=7.2 Hz, 2 H), 3.75 (s, 3H), 3.74 (s, 3H), 3.61 (m, 1H), 3.18 (m, 1H), 3.12 (d, J=16.8 Hz, 1H), 2.87 (d, J=17.4 Hz, 1H), 2.65 (m, 2H), 2.17 (m, 1H), 2.04 (m, 1H), 1.56 (s, 3H), 1.30 (t, J=7.2 Hz, 3H); HRMS (EI+) Calc'd for $C_{20}H_{26}O_6$ $[M]^+$: 362.1729. Found: 362.1724.



15f



16f

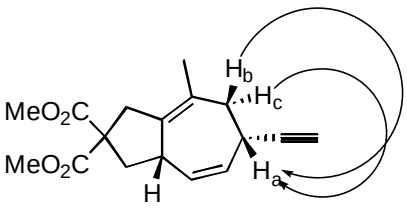
Table 3, entry 11:

***Trans*-6-ethynyl-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester 15f and *Trans*-7-ethynyl-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester** (**16f**): Alkyne **14f** (25 mg, 0.087 mmol) in 0.6 ml of distilled acetone was degassed by argon before the addition of $CpRu(CH_3CN)_3PF_6$ (4 mg, 0.009 mmol). The resulting red solution was stirred at rt for 2 h. Flash chromatography eluting with 5%-10% diethyl ether in petroleum ether afforded a mixture of **15f** and **16f** (21 mg, 0.074 mmol, 85 %, d.r.=1:2.5).

IR (film): 3288m, 2954m, 2917s, 2851m, 2112w, 1733s, 1435s, 1275s, 1257s, 1201s, 1164s, 1071m, 951w, 887w, 735w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) for major isomer **16f**: δ 5.61 (ddd, J=3.0, 6.0, 11.0 Hz, 1H), 5.49 (dt, J=2.0, 11.0 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.62 (m, 2H), 3.03 (d, J=17.0 Hz, 1H), 2.98 (d, J=17.0 Hz, 1H), 2.70 (m, 1H), 2.48 (d, J=16.0 Hz, 1H), 2.34 (m, 1H), 2.14 (d, J=2.0 Hz, 1H), 2.01 (t, J=12.0 Hz, 1H), 1.82 (s, 3H); ^{1}H-NMR (500 MHz, $CDCl_3$) for minor isomer **15f**: δ 5.61 (ddd, J=3.5, 6.5, 11.0 Hz, 1H), 5.53 (d, J=10.5 Hz, 1H),

3.76 (s, 3H), 3.75 (s, 3H), 3.48 (m, 2H), 3.04 (d, J=17.0 Hz, 1H), 2.98 (d, J=17.0 Hz, 1H), 2.70 (m, 1H), 2.64 (d, J=15.5 Hz, 1H), 2.17 (m, J=15.5 Hz, 1H), 2.10 (d, J=2.5 Hz, 1H), 2.03 (t, J=10.5 Hz, 1H), 1.74 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) for major isomer **16f**: δ 171.9, 171.8, 136.5, 132.4, 128.0, 127.5, 85.7, 69.8, 52.85, 52.76, 41.5, 39.52, 39.50, 33.7, 32.4, 28.6, 18.5; ^{13}C-NMR (125 MHz, $CDCl_3$) for minor isomer **15f**: δ 172.0, 171.9, 135.1, 132.7, 130.0, 125.5, 86.2, 68.4, 58.3, 52.8, 41.4, 39.3, 39.2, 37.5, 30.3, 29.7, 22.5; HRMS (EI+) Calc'd for $C_{17}H_{20}O_4$ $[M]^+$: 288.1362. Found: 288.1361.

COSY and nOe:

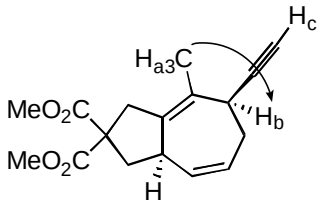


15f

δ_a = 3.48 ppm

δ_b = 2.64 ppm

δ_c = 2.17 ppm

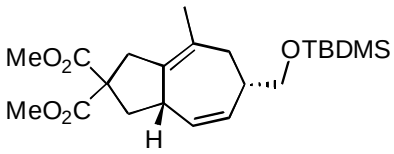


16f

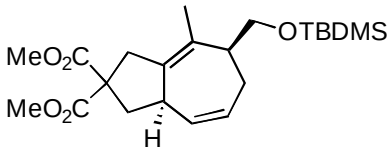
δ_a = 1.82 ppm

δ_b = 3.62 ppm

δ_c = 2.14 ppm



15g



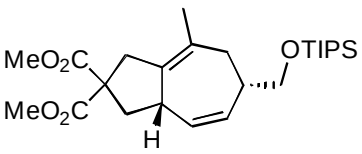
16g

Table 3, entry 12:

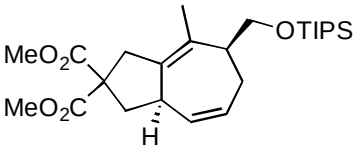
2,2-Bis(methoxycarbonyl)-8-methyl-6-(*tert*-butyldimethylsilyloxymethyl)-1,2,3,3a,6,7-hexahydroazulene (15g) and 2,2-Bis(methoxycarbonyl)-8-methyl-7-(tert-Butyl-dimethyl-silanyloxymethyl)-3,3a,6,7-tetrahydro-1H-azulene (16g):[7b] To a test tube containing $CpRu(CH_3CN)_3PF_6$ (9.5 mg, 0.022 mmol) was added a solution of vinylcyclopropane **14g** (90 mg, 0.22 mmol) in acetone (0.3 mL) and the resulting orange solution stirred at room temperature for 1 h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 10:1 petroleum ether:diethyl ether to afford a 1.5:1 mixture of **15g:16g** (81 mg, 90%) as a colorless liquid. The ratio of **15g:16g** was determined by ^{1}H-NMR integration: for **15g** a doublet of multiplets at 5.55 ppm (1H) and for **16g** a multiplet at 5.61 ppm (1H).

IR (film): 2954, 2930, 2856, 1738, 1434, 1255, 1201, 1166, 1106, 1082, 838 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.55 (dm, *J* = 11.9 Hz, 1H), 5.49 (m, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.56 (m, 1H), 3.49 (dd, *J* = 9.8 and 5.8 Hz, 1H), 3.41 (dd, *J* = 9.8 and 8.1 Hz, 1H), 2.99 (d, *J* = 16.5 Hz, 1H), 2.83 (br d, *J* = 16.5 Hz, 1H), 2.65 (ddd, *J* = 12.4, 7.9 and 1.8 Hz, 1H), 2.58 (m, 1H), 2.38 (d, *J* = 15.5 Hz, 1H), 2.42 (d, *J* = 15.5 Hz, 1H), 1.96 (t, *J* = 12.2 Hz, 1H), 1.63 (s, 3H), 0.87 (s, 9H), 0.02 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.1, 134.3, 132.9, 131.2, 127.6, 65.8, 58.3, 52.8, 52.7, 41.5, 39.9, 39.6, 39.3, 34.5, 25.9, 22.4, 18.3, -5.4, -5.3.

Additional signals for **16g**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.55 (m, 1H), 4.22 (dd, *J* = 10.9 and 5.4 Hz, 1H), 3.71 (s, 3H), 3.62 (dd, *J* = 9.9 and 5.5 Hz, 1H), 2.09 (t, *J* = 12.0 Hz, 1H), 1.98 (m, 1H), 1.44 (s, 3H), 2.34-2.28 (m, 1H), 2.13-2.07 (m, 1H), 1.83 (m, 1H).



15h



16h

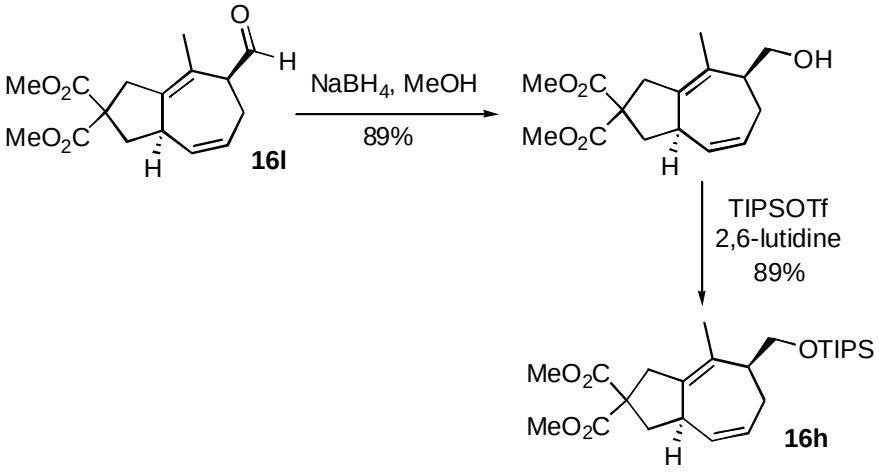
Table 3, entry 13:

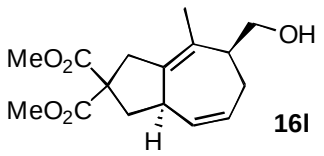
2,2-Bis(methoxycarbonyl)-8-methyl-6-(tri-*iso*-propylsilyloxymethyl)-1,2,3,3a,6,7-hexahydroazulene (**15h**): Table 3, entry 13: To a test tube containing $CpRu(CH_3CN)_3PF_6$ (2 mg, 0.005 mmol) was added a solution of vinylcyclopropane **14h** (16 mg, 0.025 mmol) in acetone (0.2 mL) and the resulting orange solution stirred at room temperature for 1 h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 5% diethyl ether:petroleum ether to afford a 3:1 mixture of **15h:16h** (13 mg, 82%) as a colorless liquid. The ratio of **15h:16h** was determined by ^{1}H-NMR integration: for **15h** a doublet at 3.02 ppm (1H) and for **16h** a multiplet at 5.64 ppm (1H).

IR (film): 2944, 2866, 1738, 1462, 1434, 1255 1200, 1164, 1106, 1069, 882 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.55 (m, 1H), 5.50 (m, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.57 (m, 3H), 3.02 (d, J = 16.7 Hz, 1H), 2.85 (br d, J = 16.7 Hz, 1H), 2.65 (dd, J = 8.0 and 1.8 Hz, 1H), 2.60 (m, 1H), 2.42 (d, *J* = 15.5 Hz, 1H), 2.00 (dd, *J* = 15.5 and 8.0 Hz, 1H) 1.95 (t, *J* = 12.1 Hz, 1H), 1.55 (s, 3H), 1.04 (m, 21H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.2, 134.3, 132.9, 131.3, 127.6, 66.1, 58.3, 52.8, 52.7, 41.5, 40.0, 39.8, 39.3, 34.5, 22.4, 18.0, 11.9; HRMS (EI+) Calc'd for $C_{24}H_{39}O_4Si$ $[M^+ - OCH_3]^+$: 419.2618. Found: 419.2626.

Table 3, entry 14: To **14h** (13 mg, 0.029 mmol) in 0.1 mL of DMF was added **4** (1.3 mg, 0.003 mmol) at rt under argon. The mixture was stirred for 5h and purified directly eluting with 5% to 15% diethyl ether in petroleum ether to afford a mixture of **15h** and **16h** (11.5 mg, 0.026 mmol, 2:1, 88%).

Verification of stereochemistry for **16h:**

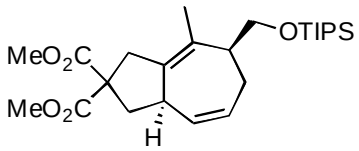




16l

2,2-Bis(methoxycarbonyl)-8-methyl-7-hydroxymethyl-1,2,3,3a,6,7-hexahydroazulene: To a solution of aldehyde **16l** (35 mg, 0.119 mmol) in methanol (1 mL) was added sodium borohydride (5 mg, 0.13 mmol). After 1h, the solution was diluted with diethyl ether (5 mL) and washed with 1 N of sodium bisulfate (2 x 5 mL), dried (magnesium sulfate) and concentrated *in vacuo*. Flash chromatography eluting with 2:1 diethyl ether: petroleum ether afforded 2,2-bis(methoxycarbonyl)-8-methyl-7-hydroxymethyl-1,2,3,3a,6,7-hexahydroazulene (31 mg, 89%) as a clear film.

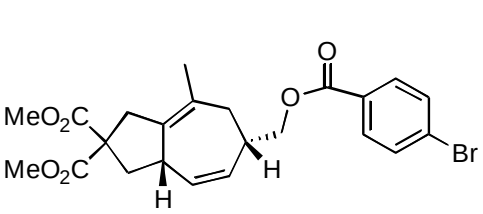
IR (film): 3401, 2955, 2857, 1737, 1436, 1258, 1204, 1169, 1092, 838, 779 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.66 (m, 1H), 5.52 (dt, *J*=10.6, 1.8 Hz, 1H), 3.76-3.71 (m, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.56 (m, 2H), 2.99 (d, *J*=16.8 Hz, 1H), 2.87 (dd, *J*=16.8, 1.8 Hz, 1H), 2.65 (ddd, *J*=12.7, 8.1, 1.8 Hz, 1H), 1.64 (s, 3H), 1.37 (brs, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.0 (2), 136.9, 133.3, 128.8, 128.7, 64.4, 58.2, 52.8, 52.7, 43.8, 41.5, 40.0, 39.5, 28.2, 17.8. HRMS (EI+) Calc'd for $C_{16}H_{22}O_5$ $[M]^+$: 294.1467. Found: 294.1468.



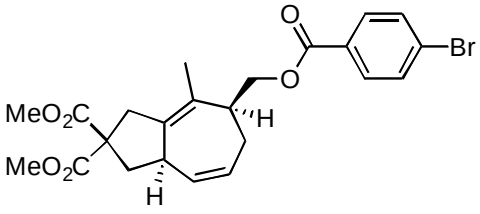
16h

2,2-Bis(methoxycarbonyl)-8-methyl-7-(tri-*iso*-propylsilyloxymethyl)-1,2,3,3a,6,7-hexahydroazulene (**16h**): To a solution of 2,2-bis(methoxycarbonyl)-8-methyl-7-hydroxymethyl-1,2,3,3a,6,7-hexahydroazulene (30 mg, 0.101 mmol) in methylene chloride (1.0 mL) was added 2,6-lutidine (35 µL, 0.30 mmol) and tri-*iso*-propylsilyl triflate (40 µL, 0.15 mmol). After stirring at room temperature for 2 h, the solution was diluted with diethyl ether (10 mL), washed with 1N sodium bisulfate (2 x 10 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 5% diethyl ether: petroleum ether afforded **16h** (41 mg, 89%) as a colorless liquid.

IR (film): 2944, 2866, 1738, 1460, 1434, 1255 1200, 1161, 1069, 882 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.64 (m, 1H), 5.50 (m, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.55 (m, 3H), 2.99 (d, *J* = 16.7 Hz, 1H), 2.82 (dd, *J* = 16.7 and 1.8 Hz, 1H), 2.63 (ddd, *J* = 12.6, 8.0 and 1.8 Hz, 1H), 2.59 (m, 1H), 2.34 (m, 1H), 2.15 (m, 1H),1.95 (t, J = 12.6 Hz, 1H), 1.56 (s, 3H), 1.03 (m, 21H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.2, 135.9, 132.8, 129.5, 129.2, 64.4, 58.2, 52.8, 52.7, 44.2, 41.5, 40.0, 39.4, 27.8, 18.2, 18.0, 12.0.



15i



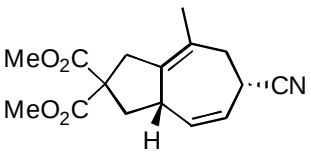
16i

Table 3, entry 15:

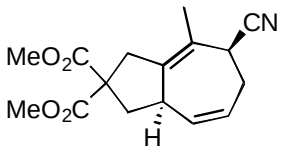
6-(4-Bromo-benzoyloxymethyl)-8-methyl-3,3a**,6,7-tetrahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester** (**15i**) **and 7-(4-Bromo-benzoyloxymethyl)-8-methyl-3,3**a**,6,7-tetrahydro-1H-azulene-2,2-dicarboxylic acid dimethyl ester** (**16i**): To a test tube containing $[CpRu(CH_3CN)_3]PF_6$ (3 mg, 0.007 mmol) was added a solution of vinylcyclopropane **14i** (35 mg, 0.073 mmol) in acetone (0.7 mL) and the resulting orange solution stirred at room temperature for 1 h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 5% diethyl ether:petroleum ether to afford a 1.6:1 mixture of **15i:16i** (25 mg, 71%) as a colorless liquid. The ratio of **15i:16i** was determined by ^{1}H-NMR integration of one of the olefinic protons: for **15i** a ddd at 5.37 ppm (1H) and for **16i** a multiplet at 5.55 ppm (1H).

R_f=0.23 (1:1 petroleum ether:ether); IR (film): 2953, 1734, 1591, 1435, 1398, 1270 1201, 1173, 1103, 1069, 1012, 757 cm^{-1}; ^{1}H-NMR (500 MHz, C_6D_6): δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 5.49 (m, 1H), 5.37 (ddd, *J* = 10.7, 5.6 and 2.6, 1H), 4.12 (dd, *J* = 10.8 and 6.1 Hz, 1H). 4.04 (dd, *J* = 10.8 and 7.8 Hz, 1H), 3.67 (m, 1H), 3.31 (s, 3H), 3.30 (s, 3H), 3.57 (m, 3H), 3.18 (d, *J* = 16.8 Hz, 1H), 2.97 (br d, *J* = 16.8 Hz, 1H), 2.79 (ddd, *J* = 12.5, 8.1 and 1.4 Hz, 1H), 2.68 (m, 1H), 2.25 (d, *J* =15.6 Hz, 1H), 2.05 (t, *J* = 12.1 Hz, 1H) 1.79 (dd, *J* = 15.4 and 8.3 Hz, 1H), 1.45 (s, 3H); ^{13}C-NMR (125 MHz, C_6D_6, both regioisomers): δ 171.8, 171.7, 165.4, 135.8, 134.3, 133.8, 131.9, 131.3, 129.7, 126.7, 67.5, 66.2, 65.7, 58.6, 52.3, 52.2, 41.0, 40.6, 42.0, 40.5, 40.0, 39.7, 34.8, 28.5, 22.3, 18.3; HRMS (EI+) Calc'd for $C_{23}H_{25}O_5Si$ $[M - CH_3]^+$: 461.0600. Found: 461.0607.

Additional signals for **16i**: ^{1}H-NMR (500 MHz, C_6D_6): δ 7.74 (d, *J* = 8.0 Hz, 2H), 5.55 (m, 1H), 4.22 (dd, *J* = 10.9 and 5.4 Hz, 1H), 4.14 (dd, *J* = 10.9 and 8.6 Hz, 1H), 3.72 (m, 1H), 3.30 (s, 3H), 3.28 (s, 3H), 2.09 (t, *J* = 12.0 Hz, 1H), 1.98 (m, 1H), 1.44 (s, 3H).



15j

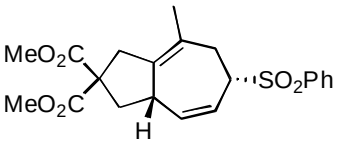


16j

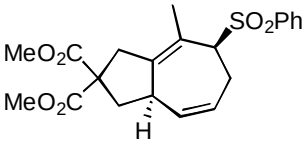
Table 3, entry 16:

***Trans*-6-cyano-8-methyl-3,3**a**,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester** (**15j**) **and *Trans*-6-cyano-8-methyl-3,3**a**,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester** (**16j**): Malonate ester **14j** (15 mg, 0.052 mmol) in 0.3 ml of distilled acetone was degassed by argon before the addition of $[CpRu(CH_3CN)_3]PF_6$ (2 mg, 0.005 mmol). The resulting brown solution was stirred at rt for 3 h. Flash chromatography eluting with 5%-10% diethyl ether in petroleum ether afforded **15j** and **16j** (13 mg, 0.045 mmol, 87%, d.r.=1:1.9). IR (film): 2921s, 2851s, 2234w, 1733s, 1456m, 1435m, 1270m, 1201m, 1165m, 1072w, 949w,

844w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) for major isomer **16j**: δ 5.68 (m, 1H), 5.60 (d, J=10.5 Hz, 1H), 3.772 (s, 3H), 3.766 (s, 3H), 3.62 (m, 1H), 3.05 (d, J=17.0 Hz, 1H), 2.95 (d, J=17.0 Hz, 1H), 2.74 (m, 1H), 2.61 (m, 1H), 2.48 (m, 1H), 2.30 (m, 1H), 2.04 (t, J=13.0 Hz, 1H), 1.88 (s, 3H); ^{1}H-NMR (500 MHz, $CDCl_3$) for minor isomer **15j**: δ 5.72 (dd, J=11.0 Hz, 1H), 5.60 (d, J=10.5 Hz, 1H), 3.768 (s, 3H), 3.766 (s, 3H), 3.56 (m, 1H), 3.05 (d, J=17.0 Hz, 1H), 2.95 (d, J=17.0 Hz, 1H), 2.74 (m, 2H), 2.64 (m, 1H), 2.20 (m, 1H), 2.05 (t, J=11.0 Hz, 1H), 1.82 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) for major isomer **16j**: δ 171.7, 171.4, 137.3, 133.4, 126.4, 123.2, 120.4, 58.1, 52.9, 41.3, 39.6, 39.2, 33.8, 32.0, 29.7, 22.7; ^{13}C-NMR (75 MHz, $CDCl_3$) for minor isomer **15j**: δ 171.8, 171.5, 139.4, 135.6, 127.5, 125.5, 122.7, 58.1, 53.0, 41.2, 39.6, 39.7, 34.9, 30.0, 29.4, 22.0; HRMS (EI+) Calc'd for $C_{16}H_{19}NO_4$ $[M]^+$: 289.1314. Found: 289.1313.



15k

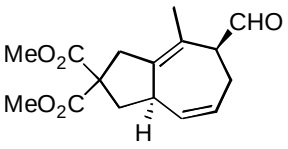


16k

Table 3, entry 17:

***Trans*-6-benzenesulfonyl-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (15k) and *Trans*-7-benzenesulfonyl-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester** (**16k**): Ester **14k** (10 mg, 0.026 mmol) in 0.3 ml of distilled acetone was degassed by argon before the addition of $[CpRu(CH_3CN)_3]PF_6$ (1.7 mg, 0.0039 mmol). The resulting dark brown solution was stirred at rt for 2 h. Without further work-up, flash chromatography eluting with 10 % to 50% diethyl ether in petroleum ether afforded a yellow oil as a mixture of **15k** and **16k** (8 mg, 0.021 mmol, 80 %). The ratio of **15k** to **16k** is 1:1.

IR (film): 2958s, 2927s, 2859s, 1732s, 1601w, 1581w, 1448m, 1381w, 1276s, 1200m, 1131s, 1074s, 957w, 724m, 691m cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) for two isomers: δ 7.87 (m, 4H), 7.57 (m, 6H), 5.82 (m, 2H), 5.57 (m, 1H), 5.32 (dt, J=10.5 Hz, 1H), 4.11 (m, 2H), 3.762 (s, 3H), 3.759 (s, 3H), 3.747 (s, 3H), 3.742 (s, 3H), 3.46 (m, 4H), 3.06 (d, J=17.0 Hz, 1H), 2.95 (m, J=16.5 Hz, 1H), 2.93 (m, J=15.0 Hz, 1H), 2.78 (dm, J=16.5 Hz, 1H), 2.59 (m, 6H), 2.03 (s, 3H), 1.71 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 171.9, 171.6, 160.3, 160.2, 144.6, 141.6, 141.5, 138.0, 137.3, 134.6, 133.6, 133.4, 133.1, 129.1, 128.8, 128.6, 126.3, 124.8, 123.0, 122.5, 70.5, 68.7, 63.4, 57.6, 52.9, 51.2, 51.0, 41.0, 40.9, 40.0, 39.3, 36.6, 31.5, 30.3, 29.7, 27.8, 27.4, 22.5; HRMS (EI+) Calc'd for $C_{15}H_{19}O_4$ $[M - C_6H_5SO_2]^+$: 263.1278. Found: 263.1267.



16l

Table 3, entry 18:

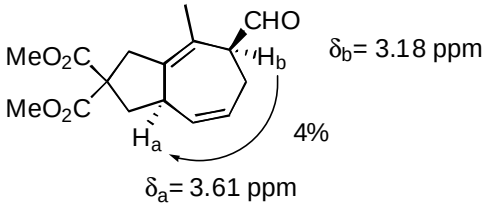
***Trans*-2,2-Bis(methoxycarbonyl)-7-formyl-8-methyl-1,2,3,3a,6,7-hexahydroazulene** (**16l**):[10]

[10] Wender, P.A.; Dyckman, A.J. *Org. Lett.* **1999**, *1*, 2089.

(72 mg, 0.25 mmol) in 0.6 mL of distilled acetone was degassed with argon for 5 min. before $[CpRu(CH_3CN)_3]PF_6$ (11 mg, 0.025 mmol) was added. The resultant yellow solution was stirred at rt. for 1 h. Flash chromatography afforded **16l** (56 mg, 0.19 mmol, 78%) as colorless oil. It was a mixture of two isomers with the ratio of 15:1. The relative stereochemistry is determined by NOE between the angular proton and α-proton of aldehyde. COSY is also obtained to confirm the structure of this compound.

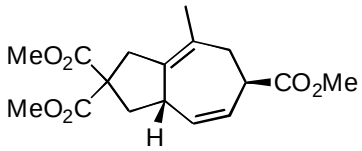
IR (film) cm^{-1}: 2955m, 2850w, 2723w, 1734s, 1437m, 1274s, 1202m, 1163m, 1078m, 953w, 885w, 822w, 804w, 749w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.67 (d, J=1.8 Hz, 1H), 5.70 (dtd, J=2.7, 6.0 and 10.2 Hz, 1H), 5.61 (dt, J=2.2 and 10.5 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.60 (m, 1H), 3.17 (m, 1H), 3.06 (d, J=17.2 Hz, 1H), 2.91 (d, J=1.8 and 17.2 Hz, 1H), 2.66 (m, 2 H), 2.32 (dt, J=5.7, 15.3 Hz, 1H), 2.04 (t, J=12.4 Hz, 1H), 1.66 (s, 3H), 1.08 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 202.8, 172.0, 171.8, 138.4, 134.5, 127.7, 124.3, 58.0, 55.0, 52.9, 52.8, 41.2, 41.0, 39.7, 26.0, 19.9; HRMS: Calc'd for $C_{16}H_{20}O_5$: 292.1311. Found: 292.1106.

nOe study:



16l

Table 4

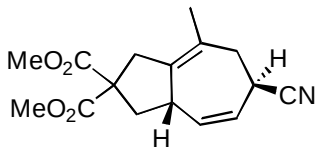


18a

Table 4, entry 1:

***Cis*-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2,6-tricarboxylic acid trimethyl ester** (**18a**):[10] Ester **17a** (15 mg, 0.047 mmol) in 0.8 ml of distilled acetone was degassed by argon before the addition of $[CpRu(CH_3CN)_3]PF_6$ (2 mg, 0.005 mmol). The resulting red solution was stirred at rt for 2 h. Flash chromatography eluting with 5%-25% diethyl ether in petroleum ether afforded **18a** (13 mg, 0.040 mmol, 87 %, a colorless oil) as a single diastereomer. The stereochemistry of the compound has been confirmed by comparison of the spectra with the known compound.[10]

^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.61 (ddd, J=2.4, 4.4, 11.7 Hz, 1H), 5.52 (ddd, J=2.3,.2.4, 11.7 Hz, 1 H), 3.73 (s, 6H), 3.70 (s, 3H), 3.55-3.60 (m, 1H), 3.14 (dm, J=12.5Hz, 1H), 2.98 (d, J=16.3 Hz, 1H), 2.86 (d, J=16.3 Hz, 1H), 2.82 (t, J=13.0 Hz, 1H), 2.73 (ddd, J=1.4, 8.4, 12.6 Hz, 1H), 2.15 (dt, J=2.2, 13.6 Hz, 1H), 1.95 (dd, J=10.8, 12.8 Hz, 1H), 1.75 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 174.3, 171.8, 137.8, 132.5, 127.5, 126.3, 58.4, 52.8, 52.7, 52.0, 42.2, 41.7, 39.9, 38.8, 35.0, 20.7.

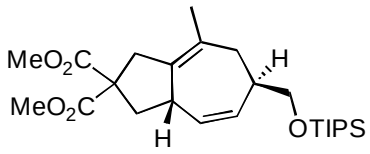


18b

Table 4, entry 2:

***Cis*-6-cyano-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester** (**18b**): Ester **17b** (21 mg, 0.073 mmol) in 0.8 ml of distilled acetone was degassed by argon before the addition of $[CpRu(CH_3CN)_3]PF_6$ (3.2 mg, 0.007 mmol). The resulting red solution was stirred at rt for 4 h. Flash chromatography eluting with 5%-25% diethyl ether in petroleum ether afforded **18b** (17 mg, 0.059 mmol, 81%) as a single diastereomer.

IR (film): 2954w, 2855w, 2238w, 1783s, 1435m, 1258s, 1204s, 1165s, 1062m, 756w, 668w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.61 (dt, J=2.5, 11.5 Hz, 1H), 5.50 (dq, J=4.0, 11.5 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.66 (bm, 1H), 3.33 (m, 1H), 2.98 (d, J=16.5 Hz, 1H), 2.93 (d, J=13.0 Hz, 1H), 2.85 (m, J=17.0 Hz, 1H), 2.73 (ddd, J=2.0, 8.5, 13.0 Hz, 1H), 2.24 (dt, J=1.5, 11.5 Hz, 1H), 1.96 (dd, J=11.0, 13.0 Hz, 1H), 1.73 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 171.61, 171.55, 138.9, 134.4, 126.4, 122.9, 120.8, 58.1, 52.9, 52.8, 41.5, 39.9, 38.9, 36.0, 29.7, 20.8; HRMS (EI+) Calc'd for $C_{16}H_{19}NO_4$ $[M]^+$: 289.1314. Found: 289.1320.

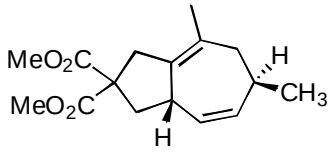


18c

Table 4, entry 3:

2,2-Bis(methoxycarbonyl)-8-methyl-6-(tri-*iso*-propylsilyloxymethyl)-1,2,3,3a,6,7-hexahydroazulene (**18c**): To a test tube containing $[CpRu(CH_3CN)_3]PF_6$ (3 mg, 0.007 mmol) was added a solution of vinylcyclopropane **17c** (33 mg, 0.073 mmol) in acetone (0.7 mL) and the resulting orange solution stirred at room temperature for 2 h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 5% diethyl ether:petroleum ether to afford **18c** (28 mg, 85%) as a colorless liquid.

IR (film): 2944, 2865, 1738, 1434, 1256 1202, 1164, 1111, 1063 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.47 (m, 1H), 5.43 (m, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.57 (dd, *J* = 9.3 and 6.0 Hz, 1H), 3.55 (m, 1H), 3.47 (dd, *J* = 9.3 and 7.5 Hz, 1H), 3.02 (d, *J* = 16.3 Hz, 1H), 2.89 (dd, *J* = 16.3 and 2.1 Hz, 1H), 2.68 (ddd, *J* = 12.4, 8.5 and 1.8 Hz, 1H), 2.44 (t, *J* = 12.4 Hz, 1H), 2.30 (m, 1H) 1.99 (ddd, *J* = 13.0, 2.0 and 1.7 Hz, 1H), 1.95 (dd, *J* = 13.0 and 11.0 Hz, 1H), 1.75 (s, 3H), 1.08 (m, 21H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.0, 136.6, 131.1, 130.6, 129.0, 68.1, 58.5, 52.7, 52.6, 42.0, 40.2, 39.5, 38.8, 37.6, 20.9, 18.0, 12.0; HRMS (EI+) Calc'd for $C_{25}H_{42}O_5Si$ $[M]^+$: 450.2802. Found: 450.2837.



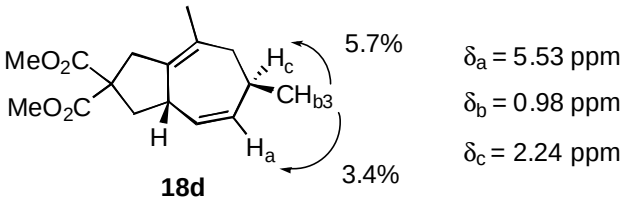
18d

Table 4, entry 4:

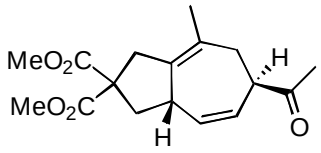
***Cis*-6,8-dimethyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (18d)**: Ester **17d** (31 mg, 0.11 mmol) in 0.5 ml of distilled acetone was degassed by argon before the addition of $[CpRu(CH_3CN)_3]PF_6$ (4.8 mg, 0.01 mmol). The resulting red solution was stirred at rt for 9 h. Flash chromatography eluting with 5%-10% diethyl ether in petroleum ether afforded **18d** (27 mg, 0.097 mmol, 87%) as a single diastereomer.

IR (film): 3001m, 2955s, 2926s, 2872m, 2852m, 1732s, 1435s, 1376w, 1268s, 1229s, 1205s, 1165s, 1117w, 1086m, 1066m, 1030w, 1002w, 953w, 887w, 822w, 753w, 689w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.33 (m, 2H), 3.744 (s, 3H), 3.738 (s, 3H), 3.55 (m, 1H), 3.00 (d, J=16.0 Hz, 1H), 2.87 (dq, J=2.0, 15.5 Hz, 1H), 2.71 (ddd, J=2.0, 8.5, 12.5 Hz, 1H), 2.46 (t, 12.5 Hz, 1H), 2.24 (m, 1H), 1.93 (dd, J=11.0, 12.5 Hz, 1H), 1.76 (m, J=2.5 Hz, 1H), 1.72 (d, J=1.0 Hz, 3H), 0.98 (d, J=7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.1, 172.0, 136.6, 135.4, 129.2, 129.1, 58.4, 52.7, 52.6, 42.0, 41.0, 39.7, 38.8, 31.1, 23.6, 21.0; HRMS (EI+) Calc'd for $C_{16}H_{22}O_4$ $[M]^+$: 278.1518. Found: 278.1512.

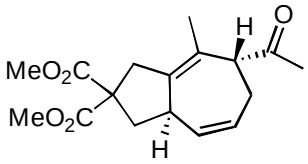
nOe study:



18d



18e



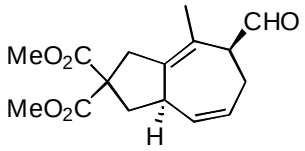
19e

Table 4, entry 5:

***Cis*-6-acetyl-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (18e) and *cis*-7-acetyl-8-methyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (19e)**: To a solution of 17e (13 mg, 0.042 mmol) in 0.5 mL of acetone was added 4 (2.0 mg, 0.0042 mmol) under argon at rt. The mixture was stirred for 4h and purified by flash chromatography eluting with 5%-20% diethyl ether in petroleum ether without workup, to afford a 2:1 mixture of 18e and 19e (12 mg, 0.039 mmol, 93%).

IR (film): 2955m, 2922w, 2859w, 1736s, 1434m, 1357w, 1261s, 1202m, 1163m, 1072w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) of major isomer **18e**: δ 5.60 (dm, J=12.0 Hz, 1H), 5.56 (dm, J=12.0 Hz, 1H), 3.76 (s, 6H), 3.60 (m, 1H), 3.15 (d, J=12.0 Hz, 1H), 3.02 (m, 1H), 2.89 (m, 1H), 2.73 (m, 2H), 2.20 (s, 3H), 2.03 (m, 2H), 1.76 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) of major isomer **18e**: δ 209.3, 171.9, 137.5, 133.3, 127.5, 126.8, 125.8, 58.4, 55.2, 52.8, 50.6, 41.7, 39.9, 39.4,

34.4, 29.7, 27.5; ^{1}H-NMR (500 MHz, $CDCl_3$) of minor isomer **19e**: δ 5.82 (ddd, J=2.5, 6.0, 11.0 Hz, 1H), 5.76 (ddd, J=1.5, 2.5, 10.5 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.61 (m, 2H), 3.04 (d, J=16.5 Hz, 1H), 2.87 (dt, J=2.0, 17.0 Hz, 1H), 2.71 (dq, J=2.5, 10.0 Hz, 1H), 2.54 (m, 1H), 2.29 (m, 1H), 2.16 (s, 3H), 2.05 (m, 1H), 1.59 (d, J=3.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) of minor isomer **19e**: δ 209.3, 172.1, 134.6, 134.3, 130.9, 128.8, 127.8, 58.2, 58.1, 52.8, 50.5, 41.2, 39.6, 39.4, 34.1, 29.7, 27.6; HRMS (EI+) Calc'd for $C_{17}H_{22}O_5$ $[M]^+$: 306.1467. Found: 306.1469.



16l

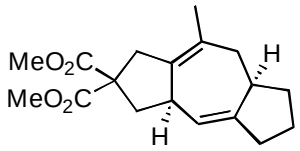
Table 4, entry 7:

***Trans*-2,2-Bis(methoxycarbonyl)-7-formyl-8-methyl-1,2,3,3**a**,6,7-hexahydroazulene** (**16l**):[10] To a test tube containing $CpRu(CH_3CN)_3PF_6$ (3 mg, 0.007 mmol) was added a solution of *cis*-vinylcyclopropane **17g** (20 mg, 0.068 mmol) in acetone (0.7 mL) and the resulting orange solution stirred at room temperature for 30 minutes. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 1:1 diethyl ether:petroleum ether to afford aldehyde **16l** (16 mg, 82%) as a 12:1 of mixture diastereomers. The ratio of diastereomers was determined by ^{1}H-NMR integration of the aldehydic proton: for the major diastereomer a doublet at 9.67 ppm (1H) and for the minor diastereomer a doublet at 9.62 ppm (1H).

IR (film): 2954, 2851, 1732, 1434, 1273, 1200, 1163, 1078, 952, 886 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.67 (d, *J* = 1.8 Hz, 1H), 5.70 (dtd, *J* = 10.2, 6.0 and 2.7 Hz, 1H), 5.61 (dt, *J* = 10.2 and 2.2 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.60 (m, 1H), 3.17 (m, 1H), 3.06 (d, *J* = 17.2 Hz, 1H), 2.91 (dd, *J* = 17.2 and 1.8 Hz, 1H), 2.66 (m, 2H), 2.32 (m, 1H) 2.04 (t, *J* = 12.4, Hz, IH), 1.66 (s, 3H), 1.08 (m, 21H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 202.8, 172.0, 171.8, 138.4, 134.5, 127.7, 124.3, 58.0, 55.0, 52.9, 52.8, 41.2, 41.0, 39.7, 26.0, 19.9; HRMS (EI+) calc'd for $C_{16}H_{19}O_5$ $[M - H]^+$: 291.1232. Found: 291.1258.

Additional signals for minor diastereomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.62 (d, *J* = 1.1 Hz, 1), 5.75 (m, 2H), 3.71 (s, 3H), 3.32 (m, 1H), 2.99 (d, *J* = 16.3 Hz, 1H), 2.83 (br d, *J* = 16.3 Hz, 1H), 2.16 (m, 1H), 1.40 (s, 3H).

Table 5



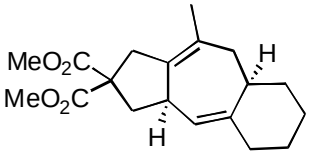
43a

Table 5, entry 1:

2,2-Bis(methoxycarbonyl)-2,3,3a,5,6,7,7a**,8-octahydro-1*H*-cyclopenta[*f*]azulene** (**43a**): To a test tube containing $CpRu(CH_3CN)_3PF_6$ (3 mg, 0.007 mmol) was added a solution of vinylcyclopropane **42a** (20 mg, 0.068 mmol) in acetone (0.4 mL) and the resulting orange solution stirred at room temperature for 1h. The reaction mixture was concentrated *in vacuo* and

chromatographed eluting with 6:1 petroleum ether: diethyl ether to afford **43a** (17 mg, 85%) as a colorless film.

IR (film): 2951, 2877, 1736, 1434, 1288, 1263, 1203, 1149, 1068 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.55 (m, 1H), 5.42 (m, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.54 (m ,1H) 3.03 (br d, *J* = 16.7 Hz, 1H), 2.91 (m, 1H), 2.88 (complex d, *J* = 16.7 Hz, 1H), 2.62 (ddd, *J* = 12.6, 8.0 and 1.6 Hz, 1H), 2.44-2.16 (m, 3H), 2.07 (t, *J* = 12.4 Hz, 1H), 1.96 (m, 2H), 1.70 (m, 1H), 1.56 (m, 1H), 1.32 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.3, 172.1, 150.0, 139.2, 122.6,, 120.6, 58.0, 52.8, 52.7, 41.8, 41.1, 39.8, 39.5, 34.4, 33.6, 33.3, 25.8; HRMS (EI+) Calc'd for $C_{17}H_{22}O_4$ $[M]^+$: 290.1518. Found: 290.1503.

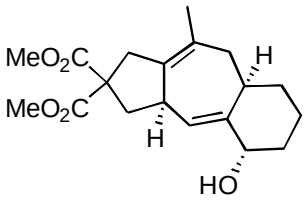


43b

Table 5, entry 2:

2,2-Bis(methoxycarbonyl)-1,2,3,3a,5,6,7,8,8a,9-decahydro-benzo[*f*]azulene (**43b**): To a test tube containing $CpRu(CH_3CN)_3PF_6$ (11 mg, 0.025 mmol) was added a solution of vinylcyclopropane **42b** (80 mg, 0.261 mmol) in acetone (1.3 mL) and the resulting orange solution stirred at room temperature for 2h. The reaction mixture was concentrated *in vacuo* and chromatographed eluting with 6:1 petroleum ether: diethyl ether to afford **43b** (65 mg, 81%) as a colorless liquid.

IR (film): 2925, 2852, 1736, 1434, 1286, 1245, 1202, 1169, 1080, 833 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.62 (m, 1H), 5.12 (br s, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.57 (m ,1H) 3.00 (ddd, *J* = 16.0, 5.3, and 26 Hz, 1H), 2.90 (dd, *J* = 16.0 and 1.1 Hz, 1H), 2.62 (ddd, *J* = 12.6, 8.6 and 1.4 Hz, 1H), 2.65 (m, 1H), 2.14 (m, 1H), 2.05 (br d, *J* = 12.8 Hz, 1H), 1.98 (dd, *J* = 12.8 and 9.9 Hz, 1H), 1.92 (m, 2H), 1.75 (m, 2H), 1.54 (m, 1H), 1.40 (m, 2H), 1.26 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 171.9, 171.8, 146.4, 143.9, 121.6,, 119.7, 59.1, 52.7, 52.6, 42.1, 40.6, 40.5, 39.0, 38.5, 33.5, 31.5, 28.7, 26.4; Anal. Calc'd for $C_{18}H_{24}O_4$; C, 71.03; H, 7.95. Found: C, 70.81; H, 7.74.



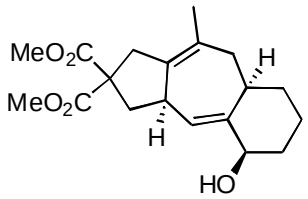
43c

Table 5, entry 3:

5-Hydroxy-10-methyl-3,3a,5,6,7,8,8a,9-octahydro-1*H*-benzo[*f*]azule-ne-2,2-dicarboxylic acid dimethyl ester (**43c**): To **42c** (3.0 mg, 0.009 mmol) in 0.5 ml of distilled acetone was added ruthenium catalyst (0.12 mg, 0.0009 mmol) at rt. The solution was stirred for 5 h. Without further work-up, flash chromatography eluting with 20% diethyl ether in petroleum ether to afford **43c** (2.4 mg, 0.0072 mmol, 80 %).

IR (film): 3415b, 2925s, 1855s, 1739s, 1434m, 1269s, 1203s, 1168m, 1122m, 1070m cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.38 (d, J=1.5 Hz, 1H), 3.88 (m, 1H), 3.750 (s, 3H), 3.747 (s, 3H), 3.57 (m, 1H), 2.93 (m, 2H), 2.78 (ddd, J=1.0, 8.5, 12.5 Hz, 1H), 2.06 (m, 3H), 1.84 (dd, J=4.0,

14.0 Hz, 1H), 1.78 (m, 1H), 1.73 (s, 3H), 1.65 (bs, 1H), 1.56 (m, 2H), 1.53 (m, 1H), 1.40 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.1, 172.0, 144.6, 137.8, 127.7, 118.8, 73.5, 58.9, 52.72, 52.86, 42.5, 39.1, 38.6, 38.1, 37.8, 32.9, 29.7, 25.6, 24.4; HRMS (EI+) Calc'd for $C_{19}H_{26}O_5$ $[M]^+$: 334.1780. Found: 334.1778.



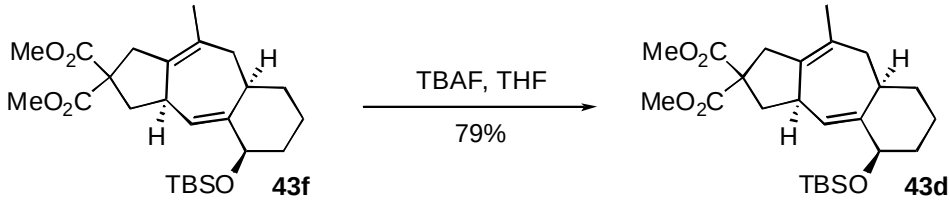
43d

Table 5, entry 4:

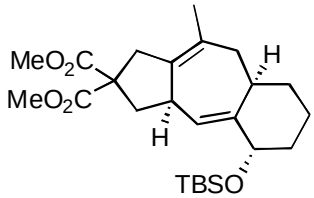
5-Hydroxy-10-methyl-3,3a,5,6,7,8,8a,9-octahydro-1*H*-benzo[*f*]azule-ne-2,2-dicarboxylic acid dimethyl ester (**43d**): To **42d** (8.0 mg, 0.024 mmol) in 0.2 ml of distilled acetone was added ruthenium catalyst (1.0 mg, 0.0024 mmol) at rt. The solution was stirred for 4 h. Without further work-up, flash chromatography eluting with 20% to 50% diethyl ether in petroleum ether to afford **43d** (5.6 mg, 0.017 mmol, 81 %).

IR (film): 3408b, 2926s, 2855m, 1736s, 1434m, 1268s, 1203s, 1162m, 1121m, 1169m cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.34 (bs, 1H), 4.10 (dd, J=2.5, 3.0 Hz, 1H), 3.75 (s, 6H), 3.56 (m, 1H), 2.93 (d, J=1.0 Hz, 2H), 2.84 (d, J=14. 5 Hz, 1H), 2.73 (ddd, J=1.0, 9.0, 13.0 Hz, 1H), 2.65 (m, 1H), 1.97 (dd, J=9.0, 13.0 Hz, 1H), 1.87 (m, 1H), 1.80 (dd, J=4.0, 14.0 Hz,1H), 1.73 (d, J=1.5 Hz, 3H), 1.58 (m, 1H), 1.53 (m, 2H), 1.44 (m, 1H), 1.32 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.0, 143.9, 137.4, 128.0, 126.0, 76.1, 58.9, 52.74, 52.66, 42.3, 38.6, 38.5, 37.8, 34.7, 34.6, 33.3, 30.3, 29.7; HRMS (EI+) Calc'd for $C_{19}H_{26}O_5$ $[M]^+$: 334.1780. Found: 334.1778.

Verification of Stereochemistry for **43d**:



To **43f** (15 mg, 0.033 mmol) in 1 mL of distilled THF was added 1M TBAF solution (0.33 ml) in THF at 50 °C and stirred for 6 h. The resulting solution was stirred at rt for additional 12 h and separated by flash chromatography eluting with 50% diethyl ether in petroleum ether to afford **43d** (9.0 mg, 0.026 mmol, 79%).

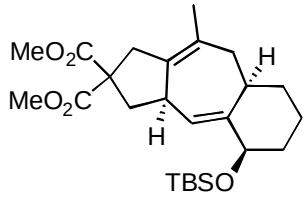


43e

Table 5, entry 5:

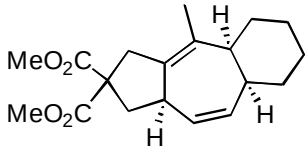
5-(*tert*-Butyldimethylsilyloxy)-10-methyl-3,3a,5,6,7,8,8a,9-octahydro-1*H*-benzo[*f*]azule-ne-2,2-dicarboxylic acid dimethyl ester (**43e**): To **42e** (13 mg, 0.029 mmol) in 0.5 ml of distilled acetone was added ruthenium catalyst (1.3 mg, 0.0029 mmol) at rt. The solution was stirred for

2 h. Without further work-up, flash chromatography eluting with 5% to 20% diethyl ether in petroleum ether to afford **43e** (9 mg, 0.020 mmol, 69 %).
IR (film): 2929s, 2856s, 1737s, 1460m, 1434m, 1266s, 1202m, 1154m, 1128m, 1084m, 952w, 910w, 888w, 836m, 776w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.40 (bs, 1H), 3.80 (m, 1H), 3.75 (s, 6H), 3.55 (m, 1H), 2.92 (m, 2H), 2.74 (ddd, J=1.0, 8.5, 12.5 Hz, 1H), 2.05 (dd, J=9.5, 12.5 Hz, 1H), 2.00 (m, 1H), 1.91 (m, 1H), 1.82 (dd, J=4.0, 13.0 Hz, 1H), 1.76 (m, 1H), 1.72 (s, 3H), 1.55 (m, 1H), 1.48 (m, 2H), 1.32 (m, 2H), 0.92 (s, 9H), 0.066 (s, 3H), -0.058 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.2, 172.0, 143.9, 138.1, 127.4, 119.4, 74.2, 59.0, 52.7, 52.6, 42.5, 39.4, 38.6, 38.5, 38.0, 33.0, 29.7, 25.9, 24.6, 22.5, 18.4, -4.83, -4.97; HRMS (EI+) Calc'd for $C_{25}H_{40}O_5Si$ $[M]^+$: 448.2645. Found: 448.2648.



43f

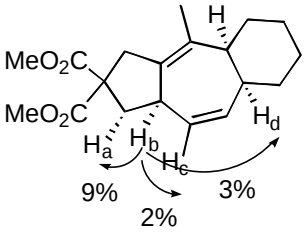
Table 5, entry 6:
5-(*tert*-Butyldimethylsilyloxy)-10-methyl-3,3a,5,6,7,8,8a,9-octahydro-1*H*-benzo[*f*]azule-ne-2,2-dicarboxylic acid dimethyl ester (**43f**): To **42f** (27 mg, 0.060 mmol) in 0.5 ml of distilled acetone was added ruthenium catalyst (2.6 mg, 0.006 mmol) at rt. The solution was stirred for 5 h. Without further work-up, flash chromatography eluting with 5% to 20% diethyl ether in petroleum ether to afford **43f** (22 mg, 0.049 mmol, 81 %).
IR (film): 2930s, 2857s, 1740s, 1435w, 1251s, 1202m, 1168m, 1107m, 1078s, 1034m, 966w, 915w, 836m, 775m cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.17 (bs, 1H), 4.00 (t, J=2.5 Hz, 1H), 3.74 (s, 6H), 3.53 (bm, 1H), 2.93 (m, 2H), 2.79 (d, J=3.5 Hz, 1H), 2.72 (ddd, J=1.0, 8.5, 13.0 Hz, 1H), 2.61 (m, 1H), 1.94 (dd, J=10.0, 13.0 Hz, 1H), 1.86 (dt, J=4.0, 9.0 Hz, 1H), 1.77 (m, 2H), 1.72 (d, J=1.0 Hz, 3H), 1.59 (m, 2H), 1.48 (m, 1H), 1.36 (m, 1H), 0.90 (s, 9H), 0.036 (s, 3H), 0.019 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.1, 145.1, 137.1, 128.1, 123.5, 76.4, 58.9, 52.7, 52.6, 42.4, 38.63, 38.59, 37.8, 36.3, 34.7, 33.3, 25.8, 22.7, 20.8, 18.1, -4.48, -5.07; HRMS (EI+) Calc'd for $C_{25}H_{40}O_5Si$ $[M]^+$: 448.2645. Found: 448.2644.



43g

Table 5, entry 7:
4-Methyl-3-4a,5,6,7,8,8a,10a-octahydro-1*H*-benzo[*f*]azulene-2,2-dicarboxylic acid dimethyl ester (**43g**): Malonate ester **42g** (30 mg, 0.094 mmol) in 0.5 ml of distilled acetone was degassed by argon before the addition of ruthenium catalyst (4 mg, 0.009 mmol). The resulting red solution was stirred at rt for 6 h. Without workup, flash chromatography of the reaction mixture eluting with 5%-10% diethyl ether in petroleum ether afforded yellow oil that is the single diastereomer of the tricyclic compound **43g** (28 mg, 0.088 mmol, 93 %).
IR (film): 3024w, 2929s, 2855s, 1738s, 1434m, 1380w, 1271s, 1233m, 1201m, 1164m, 1141m, 1075m, 952w, 889w, 823w, 748w, 685w cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.69 (bs, 2H), 3.74 (s, 3H), 3.72 (s, 3H), 3.48 (m, 1H), 3.05 (d, J=16.8 Hz, 1H), 3.05 (m, 1H), 2.77 (d, J=17.4

Hz, 1H), 2.60 (dd, J=7.5, 12.3 Hz, 1H), 2.04 (t, J=12.6 Hz, 1H), 1.82 (d, J=11.1 Hz, 1H), 1.74 (d, J=12.3 Hz, 1H), 1.65 (m, 4H), 1.55 (s, 3H), 1.42 (m, 1H), 1.25 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): 172.3, 133.9, 133.0, 132.1, 130.7, 57.9, 52.8, 52.7, 47.0, 41.3, 40.2, 39.6, 39.0, 36.5, 31.4, 27.2, 21.5, 21.0; HRMS (EI+): Calc'd for $C_{19}H_{26}O_4$ $[M]^+$: 318.1831. Found: 318.1821.
nOe and COSY:



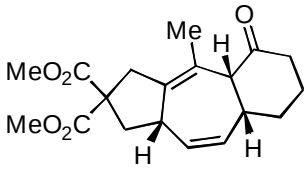
δ_a = 2.59 ppm

δ_b= 3.48 ppm

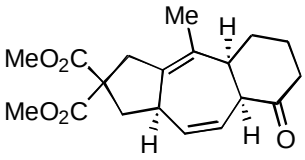
δ_c = 5.69 ppm

δ_d = 3.05 ppm

43g



43h

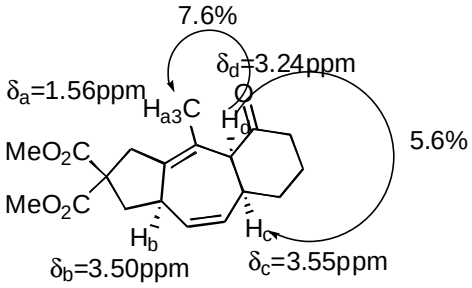


43h'

Table 5, entry 8:

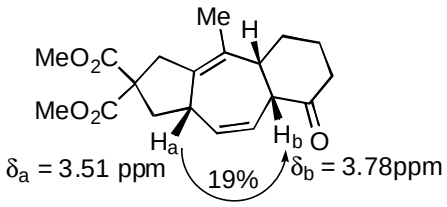
4-Methyl-5-oxo-3,4a,5,6,7,8,8a,10a-octahydro-1*H*-benzo[*f*]azulene-2,2-dicarboxylic acid dimethyl ester (**43h**) **and 4-Methyl-8-oxo-3,4a,5,6,7,8,8a,10a-octahydro-1*H*-benzo[*f*]azulene-2,2-dicarboxylic acid dimethyl ester** (**43h'**): To **42h** (32 mg, 0.096 mmol) in 0.5 ml of distilled acetone was added ruthenium catalyst (4 mg, 0.0096 mmol) at rt. The solution was stirred for 4 h at rt. Without further work-up, flash chromatography eluting with 1% to 5% diethyl ether in petroleum ether afforded **43h** and **43h'** (16 mg, 0.074 mmol, 84 %, **43h**:**43h'**=6:1).

For major isomer **43h**: IR (film): 3008w, 2953m, 2923m, 2852w, 1736s, 1689s, 1437m, 1329w, 1287m, 1246m, 1210s, 1123w, 1066m, 1031w, 967w, 899w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.76 (dt, J=10.0, 2.5 Hz, 1H), 5.52 (ddd, J=2.5, 6.5, 9.5 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.55 (bs, 1H), 3.50 (m, 1H), 3.24 (bs, 1H), 3.10 (d, J=17.5 Hz, 1H), 2.97 (dd, J=1.5, 17.5 Hz, 1H), 2.61 (ddd, J=2.0, 8.0, 12.5 Hz, 1H), 2.39 (m, 2H), 2.14 (t, J=12.5 Hz, 1H), 2.08 (m, 2H), 1.90 (m, 1H), 1.84 (m, 1H), 1.56 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 210.5, 172.3, 171.8, 135.2, 134.9, 129.9, 124.6, 59.1, 57.8, 52.8, 52.7, 42.3, 40.7, 40.6, 39.71, 39.65, 30.0, 24.1, 22.3; HRMS (EI+) Calc'd for $C_{19}H_{24}O_5$ $[M]^+$: 332.1624. Found: 332.1622.
nOe study:



43h

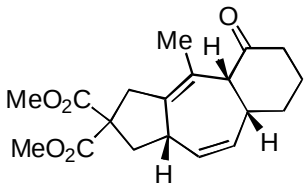
For minor isomer **43h'**: IR (film) cm^{-1}: 2959s, 2923s, 2855m, 1734s, 1722s, 1434m, 1378w, 1257s, 1120m, 1164m, 1122w, 1099w, 1072w, 1048w, 965w, 984w, 803w, 747w, 668w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.89 (dt, J=9.5, 3.0 Hz, 1H), 5.61 (ddd, J=3.0, 5.5, 9.5 Hz, 1H), 3.72 (s, 3H), 3.76 (s, 3H), 3.55 (bs, 1H), 3.08 (d, J=17.0 Hz, 1H), 2.94 (dd, J=17.0 Hz, 1H), 2.71 (dd, J=6.5, 13.5 Hz, 1H), 2.65 (ddd, J=2.0, 7.5, 12.5 Hz, 1H), 2.34 (d, J=12.5 Hz, 1H), 2.21 (m, 1H), 2.09 (m, 2H), 1.87 (m, 1H), 1.67 (m, 1H), 1.62 (m, 2H), 1.46 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 212.1, 183.1, 172.0, 136.6, 133.6, 128.8, 127.8, 57.8, 54.9, 52.9, 47.8, 41.0, 40.3, 39.5, 37.8, 29.7, 26.0, 25.9, 21.2; ^{1}H-NMR (500 MHz, C_6D_6): δ 5.61 (ddd, J=3.0, 3.0, 10.0 Hz, 1H), 5.29 (dddd, J=3.0, 5.5, 10.0 Hz, 1H), 3.78 (bs, 1H), 3.51 (bs, 1H), 3.30 (s, 3H), 3.29 (s, 3H), 3.20 (d, J=12.0 Hz, 1H), 2.67 (d, 17.5 Hz, 1H), 2.83 (dd, J=1.5, 17.5 Hz, 1H), 2.67 (ddd, J=1.5, 7.5, 12.0 Hz, 1H), 2.19 (m, 1H), 2.10 (m, 2H), 1.22 (bd, J=12.0 Hz, 1H), 1.48 (m, 1H), 1.45 (m, 5H). HRMS (EI+) Calc'd for $C_{19}H_{24}O_5$ $[M]^+$: 332.1624. Found: 332.1620.
nOe study:



43h'
in C_6D_6

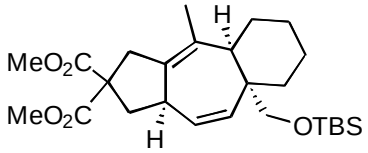
Chemical shift study:

	No Eu(fod)$_3$	5% Eu(fod)$_3$	10% Eu(fod)$_3$
43h'(allylic methyl)	1.596	1.615(+0.019)	1.632(+0.017)
43h (allylic methyl)	1.541	1.562(+0.021)	1.587(+0.025)
43h' (olefinic proton adjacent to cyclohexanone)	5.582	5.638(+0.056)	5.690(+0.052)
43h (olefinic proton adjacent to cyclohexanone)	5.503	5.519(+0.016)	5.538(+0.019)



43h

Table 5, entry 9:
With In(OTf)3: To a solution of **42h** (12 mg, 0.036 mmol) in 0.5 mL of acetone was added **4** (1.5 mg, 0.0036 mmol) and In(OTf)$_3$ (9 mg, 0.018 mmol) under argon at rt. The mixture was stirred for 4h and purified by flash chromatography eluting with 5%-20% diethyl ether in petroleum ether without workup, to afford **43h** (9.3 mg, 0.028 mmol, 78%).



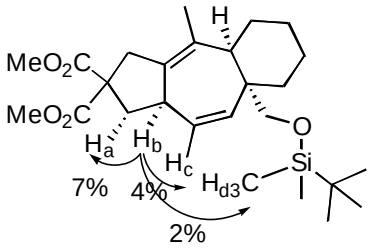
43i

Table 5, entry 10:

8a-(*tert*-Butyldimethylsilyloxymethyl)-4-Methyl-3-4a,5,6,7,8,8a,10a-octahydro-1*H*-benzo[*f*]azulene-2,2-dicarboxylic acid dimethyl ester (**43i**): To malonate ester **42i** in 0.5 mL of acetone was added catalyst (2 mg, 0.004 mmol). The resulting red solution was stirred at rt 3 h. Without workup, flash chromatography of the reaction mixture eluting with 5%-10% diethyl ether in petroleum ether afforded a yellow oil isolated as a single diastereomer of the tricyclic compound **43i** (16 mg, 0.035 mmol, 85 %).

IR (film): 2930s, 2857s, 1768s, 1462w, 1435w, 1258s, 1197m, 1162m, 1108m, 1076m, 1007w, 939w, 837m, 775m, 667w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.63 (d, J=11.5 Hz, 1H), 5.36 (d, J=11.0 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.35 (d, J=9.5 Hz, 1H), 3.24 (m, J=11.0 Hz, 1H), 2.99 (d, J=17.5 Hz, 1H), 2.88 (d, J=17.5 Hz, 1 H), 2.53 (dd, J=6.5, 14.0Hz, 1H), 1.98 (m, 2H), 1.70 (m, J=8.0Hz, 2H), 1.64 (s, 3H), 1.60 (m, 1H), 1.51 (m, 2H), 1.22 (m, 4H), 0.89 (s, 9H), -0.004 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 172.7, 172.5, 134.7, 130.1, 130.0, 128.3, 66.4, 56.8, 52.79, 52.75, 47.9, 45.3, 42.7, 41.6, 39.7, 36.4, 30.1, 27.3, 25.9, 22.5, 22.2, 18.3, -5.59, -5.72; HRMS (EI+) Calc'd for $C_{22}H_{33}O_5Si$: 405.2097. Found: 405.2103. Anal. Calc'd for $C_{26}H_{42}O_5Si$ $[M]^+$: C, 67.49; H, 9.16. Found: C, 67.35; H, 9.33.

nOe data:



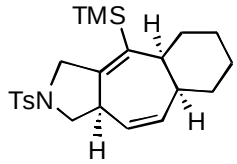
δ_a = 2.99 ppm

δ_b= 3.25 ppm

δ_c= 5.61 ppm

δ_d= 0.89 ppm

43i



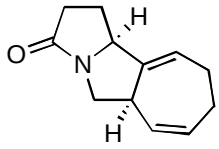
43j

Table 5, entry 11:

2-(Toluene-4-sulfonyl)-4-trimethylsilyl-1,2,3,4a,5,6,7,8,8a,10a-decahydro-2-aza-benzo-[*f*]azulene (**43j**): To **42j** (14 mg, 0.039 mmol) in 0.5 ml of distilled acetone was added ruthenium catalyst (1.7 mg, 0.004 mmol) at rt. The solution was stirred for 8h at rt. Without further work-up, flash chromatography eluting with 5% diethyl ether in petroleum ether afforded **43j** (16 mg, 0.074 mmol, 84 %).

IR (film): 2919s, 2850m, 1599w, 1447w, 1350m, 1250w, 1161s, 1094m, 1044w, 869w, 836m, 667s cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.73 (d, J=8.5 Hz, 1H), 7.37 (d, J=8.0 Hz, 1H), 5.71 (m, 1H), 5.53 (dt, J=2.5, 10.5 Hz, 1H), 4.07 (d, J=2.0, 13.0 Hz, 1H), 3.71 (m, 2H), 3.58 (dt, J=2.0 Hz, 13.5 Hz, 1H), 3.07 (bs, 1H), 2.76 (dd, J=8.0, 10.0 Hz, 1H), 2.47 (s, 3H), 2.12 (d, J=10.0 Hz, 1H), 0.94-0.67 (m, 10H), 0.59 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 143.7, 142.8, 137.1,

135.9, 132.2, 129.7, 128.8, 127.9, 53.44, 53.38, 43.8, 42.3, 37.2, 31.9, 29.8, 26.9, 21.6, 21.1, 0.25; HRMS (EI+) Calc'd for $C_{23}H_{33}NO_2Si$ $[M]^+$: 415.2001. Found: 415.2003.



43k

Table 5, entry 12:

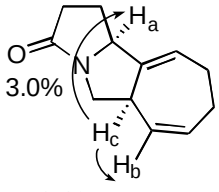
3,3a,6,8a,9-Hexahydro-2*H*-9a-aza-cyclopenta[*a*]azulen-1-one (**43k**): To **42k** (16 mg, 0.085 mmol) in 0.5 ml of distilled acetone was added ruthenium catalyst (6 mg, 0.013 mmol) at 50°C. It was stirred at 50°C for 11h. Without further work-up, flash chromatography eluting with 5% to 30% ethyl acetate in petroleum ether afforded **43k** (11.5 mg, 0.061 mmol, 72%(75% brsm)).

IR (film): 2923s, 2851s, 1686s, 1561w, 1459m, 1415s, 1284m, 1232w, 1165w, 1075w, 1041w, 969w, 826w, 729w, 671w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.83 (m, 1H), 5.67 (m, 1H), 5.52 (m, 1H), 4.44 (tm, J=7.5 Hz, 1H), 4.25 (dd, J=9.0, 11.5 Hz, 1H), 3.84 (m, 1H), 2.76 (t, J=11.0 Hz, 1H), 2.66 (dtm, J=9.5, 16.0 Hz, 1H), 2.40 (m, 5H), 2.15 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 175.7, 145.8, 131.2, 129.5, 122.2, 47.9, 41.9, 33.5, 29.7, 28.8, 26.1, 25.4; HRMS (EI+) Calc'd for $C_{12}H_{15}NO$ $[M]^+$: 189.1154. Found: 189.1147. nOe study:

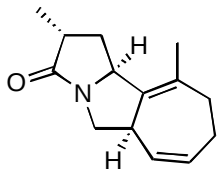
δ_a = 4.44 ppm

δ_b = 5.52 ppm

δ_c = 3.84 ppm



43k



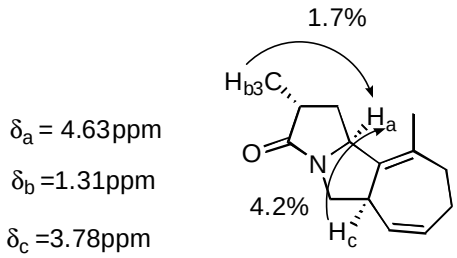
43l

Table 5, entry 13:

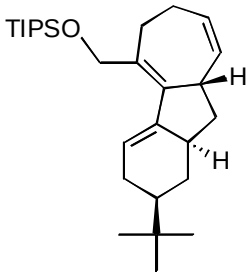
2,4-Dimethyl-3,3a,5,6,8a,9-hexahydro-2*H*-9a-aza-cyclopenta[*a*]azulen-1-one (**43l**): To **42l** (19 mg, 0.088 mmol) in 0.5 ml of distilled acetone was added ruthenium catalyst (3.8 mg, 0.09 mmol) at rt. The solution was stirred for 7 h at rt. Without further work-up, flash chromatography eluting with 1% to 5% diethyl ether in petroleum ether to afford **43l** (16 mg, 0.074 mmol, 84 %).

IR (film): 2965s, 2930w, 2873s, 1694s, 1454s, 1423s, 1372m, 1338w, 1284m, 1254w, 1231w, 960w, 795w, 767w, 730w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.78 (m, 1H), 5.46 (m, 1H), 4.63 (t, J=7.5 Hz, 1H), 4.24 (dd, J=9.5 Hz, 11.5 Hz, 1H), 3.78 (m, 1H), 2.73 (dd, J=10.5, 11.5 Hz, 1H), 2.59 (m, 1H), 2.45 (m, 1H), 2.34 (m, 1H), 2.19 (m, 2H), 2.02 (m, 2H), 1.68 (t, J=1.5 Hz, 3H), 1.31 (d, J=7.5 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 177.6, 138.3, 130.8, 130.3, 129.6, 61.6, 48.1, 42.0, 40.3, 36.9, 32.5, 25.6, 21.3, 17.5; HRMS (EI+) Calc'd for $C_{14}H_{19}NO$ $[M]^+$: 217.1467. Found: 217.1461.

nOe study:



43l



43m

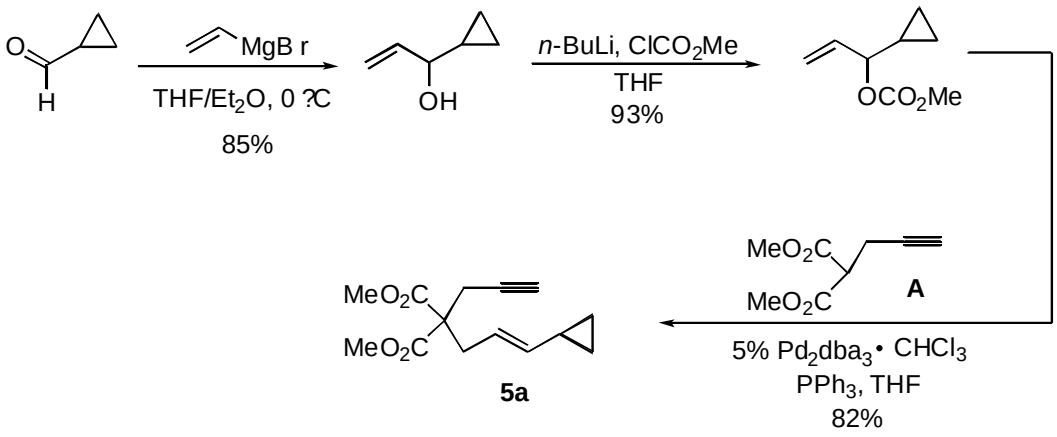
Table 5, entry 14:

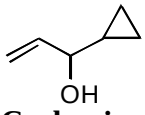
(2-*tert*-Butyl-1,2,3,6,7,9a**,10,10**a**-octahydro-benzo[*a*]azulen-5-ylmethoxy)-triisopropyl-silane** (**43m**): To **42m** (43 mg, 0.10 mmol) in 0.5 ml of distilled acetone was added ruthenium catalyst (4.3 mg, 0.01 mmol) at rt. The solution was stirred 3 h. Without further work-up, flash chromatography eluting with 1% to 5% diethyl ether in petroleum ether afforded **43m** (39 mg, 0.091 mmol, 91 %).

IR (film): 2944s, 2867s, 1717w, 1654w, 1464m, 1384w, 1366m, 1259w, 1097s, 1069m, 1014m, 996m, 920w, 882m, 775m, 683s cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.58 (m, 1H), 5.55 (m, 1H), 5.34 (ddd, J=2.0, 4.0, 11.5 Hz, 1H), 4.70 (d, J=12.0 Hz, 1H), 4.35 (dd, J=2.0, 12.5 Hz, 1H), 3.68 (m, 1H), 2.65 (m, 2H), 2.21 (m, 5H), 2.03-1.80 (m, 5H), 1.15 (m, 21H), 0.85 (m, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 141.7, 141.3, 136.3, 131.8, 128.8, 122.5, 63.0, 52.4, 43.9, 41.0, 40.8, 40.5, 32.2, 30.9, 28.0, 27.6, 27.3, 27.2, 26.9, 18.04, 18.01, 17.98, 17.95, 17.87, 12.0, 11.9; HRMS (EI+) Calc'd for $C_{28}H_{48}OSi$ $[M]^+$: 428.3474. Found: 428.3474.

Part II:
Preparation of substrates:

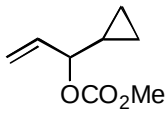
Substrates in Table 1:
5a:





Carbonic acid 1-cyclopropyl-allyl ester methyl ester: To a solution of 1.0M vinylmagnesium bromide in THF (15 mL, 15 mmol) at 0 ºC was slowly added a solution of cyclopropanal (1 mL, 13.4 mmol) in diethyl ether (15 mL). After stirring at 0 ºC for 1 h, the solution was diluted with diethyl ether (100 ML), washed with 1N hydrochloric acid (2 x 50 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Kugelrohr distillation (oven temp 90 ºC) affords 1-cycloproylpro-2-en-1-ol (1.11 g, 85%) as a colorless liquid.

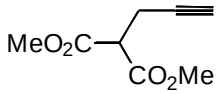
^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.92 (ddd, *J* = 17.2, 10.6 and 6.7 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.08 (d, *J* = 10.6 Hz, 1H), 3.43 (t, *J* = 6.7 Hz, 1H), 2.15 (br s, 1H), 0.95 (m, 1H), 0.51 (m, 2H), 0.33 (m, 1H), 0.23 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 139.5, 114.5, 77.1, 12.2, 3.0, 1.9.



Methyl (1-cyclopropylpro-2-en-1-yl)carbonate: To a solution of the above alcohol (300 mg, 3.06 mmol) in THF (5 mL), at 0 ºC, was slowly added 1.0M *n*-butyllithium (3.4 mL, 3.4 mmol). After stirring at 0 ºC for 30 min., methyl chloroformate (0.35 mL, 4.5 mmol) was added and the solution warmed to rt. After an additional 1 h, the reaction mixture was diluted with diethyl ether (25 mL) and washed with 1N hydrochloric acid (2 x 25 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 10:1 petroleum ether:diethyl ether afforded methyl (1-cyclopropylpro-2-en-1-yl)carbonate (444 mg, 93%) as a colorless liquid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.85 (ddd, *J* = 17.4, 10.6 and 6.2 Hz, 1H), 5.30 (d, *J* = 17.4 Hz, 1H), 5.18 (d, *J* = 10.6 Hz, 1H), 3.50 (dd, *J* = 8.6 and 6.4 Hz, 1H), 3.75 (s, 3H), 1.12 (m, 1H),

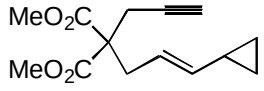
0.57 (m, 2H), 0.46 (m, 1H), 0.31 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 155.3, 134.8, 117.1, 83.0, 54.5, 14.4, 3.5, 2.3.



A

2-Prop-2-ynyl-malonic acid dimethyl ester:[11] To a flask with NaH (802 mg, 20 mmol) in 40 mL THF was added dimethylmalonate (2.7 g, 20.5 mmol). The solution was cooled to 0 °C and propargyl bromide (1.48g, 80% in toluene, 10 mmol) was added. The reaction was stirred 12 h at 4 °C, then extracted with 50 mL saturated aqueous NH_4Cl and 50 mL saturated aqueous NaCl. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by slash chromatography (silica gel, 5:1 PE:Et_2O) to give malonate **A** (0.76 g, 4.47 mmol, 44% yield) as a clear, colorless oil.

R_f=0.42 (2:1 PE:Et_2O); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.74 (s, 6H), 3.61 (t, J=7.7 Hz, 1H), 2.80 (dd, J=7.8, 2.6 Hz, 2H), 2.04 (t, J=3.0 Hz, 1H).



5a

4,4-Bis(methoxycarbonyl)-7-cyclopropyl-hept-6(*E*)-en-1-yne (**5a**):[12] To a degassed flask containing Pd_2dba_3•$CHCl_3$ (60 mg, 0.058 mmol) and triphenylphosphine (60 mg, 0.343 mmol) was added THF (3 mL). After stirring at rt for 10 min., to the resulting orange solution was added a solution of alkyne **A** (215 mg, 1.26 mmol) and methyl (1-cyclopropylpro-2-en-1-yl)carbonate (180 mg, 1.15 mmol) in THF (3 mL). After an additional 12 h, the solution was concentrated *in vacuo* and chromatographed eluting with 10:1 petroleum ether:diethyl ether to afford **5a** (260 mg, 82%) as a colorless liquid.

IR (film): 3290, 3005, 2954, 1737, 1438, 1291, 1202, 964 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.28 (dt, J = 15.1 and 7.5 Hz, 1H), 5.12 (dd, J = 15.1 and 8.8 Hz, 1H), 3.75 (s, 6H), 2.80 (d, J = 2.8 Hz, 2H), 2.74 (d, J = 7.6 Hz, 2H), 2.02 (t, J = 2.8 Hz, 1H), 1.35 (m, 1H), 0.68 (m, 2H), 0.33 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.3, 139.7, 120.0, 78.9, 71.3, 57.1, 52.7, 35.1, 22.4, 13.6, 6.6; Anal. Calc'd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.89; H, 7.10.

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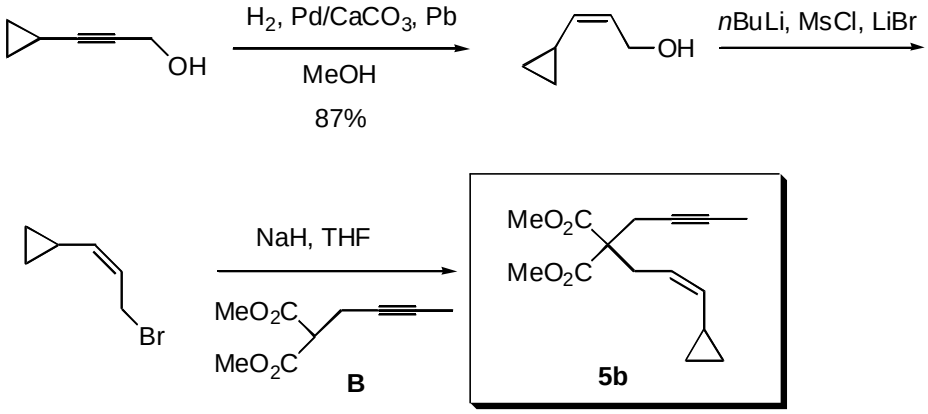
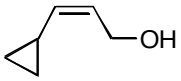
[11] Wender, P.A.; Dyckman, A.J.; Husfeld, C.O.; Kadereit, D.; Love, J.A.; Rieck, H. *J. Am. Chem. Soc.* **1999**, *121*, 10442.

[12] a. Wender, P.A.; Sperandio, D. *J. Org. Chem.* **1998**, *63*, 4164. b. Wang, B.; Cao, P.; Zhang, X. *Tetrahedron Lett.* **2000**, *41*, 8041.

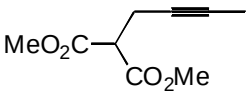
5b:



79% over 2 steps

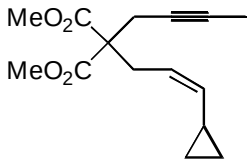


(*Z*)-3-cyclopropyl-2-propen-1-ol: To 3-cyclopropyl-2-propyn-1-ol (1.0 g, 10.4 mmol) in 4 mL of distilled methanol was added Lindlar catalyst (5% $Pd/CaCO_3$/Pb, 100 mg). To this solution was bubbled hydrogen gas from a balloon through a needle at rt. for 7h. After seven hours, the solution was concentrated to about 2mL (not completely dry!) and separated via flash chromatography eluting with 10% to 50% diethyl ether in petroleum ether to afford Z-3-cyclopropyl-2-propen-1-ol as a mixture of cis and trans isomers in >10:1 ratio (0.89 g, 9.1 mmol, 87%).
IR (film) cm^{-1}:3331s, 3083m, 3007s, 2931m, 2871m, 1656w, 1431w, 1311w, 12272, 1045s, 1021s, 958s, 931m, 884w, 811w, 737w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.54 (dt, J=7.0, 11.0 Hz, 1H), 4.90 (dd, J=10.0, 11.0 Hz,1H), 4.32 (dd, J=1.5, 8.0 Hz, 2H), 1.83 (bs, 1H), 1.61 (m, 1H), 0.77 (m, 2H), 0.40 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 137.4, 126.3, 58.9, 9.76, 7.13; Anal. Calc'd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.36; H, 10.13.



B

2-But-2-ynyl-malonic acid dimethyl ester:[11] To a flask with NaH (806 mg, 20.2 mmol) in 40 mL THF was added dimethylmalonate (2.70 g, 20.4 mmol). The solution was cooled to 0 °C and 1-bromo-2-butyne (863 mg, 6.49 mmol) was added. The reaction was stirred 12 h at 4 °C, then extracted with 50 mL saturated NH_4Cl and 50 mL brine. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by slash chromatography (silica gel, 4:1 PE:Et_2O) to give malonate **B** (0.70 g, 3.80 mmol, 59% yield) as a clear, colorless oil.
R_f=0.42 (2:1 PE:Et_2O; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 6H), 3.56 (t, J=7.5 Hz, 1H), 2.72 (m, 2H), 1.73 (t, J=2.3 Hz, 1H).

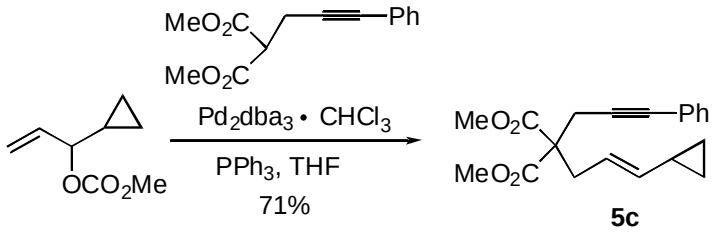


5b

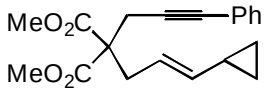
Dimethyl *cis*-2-but-2-ynyl-2-(3-cyclopropylallyl)-malonate (**5b**): To a slurry of sodium hydride (60%, 10 mg, 0.26mmol) in 0.5 mL of THF was added a solution of malonate ester **B** (42 mg, 0.23 mmol) in 1 mL of THF at 0°C. This suspension was stirred for 25 min. To another flask was added (*Z*)-3-cyclopropyl-2-propen-1-ol (23 mg, 0.23 mmol) and 0.5 mL of distilled THF. To this solution was added *n*-butyllithium (1.6 M in hexane, 0.16 mL, 0.26 mmol) at -78°C and stirred for 30 min followed by the addition of methanesulfonyl chloride (29 mg, 20 uL, 0.26 mmol) and 5 mg of lithium bromide. At -78 °C the mixture was stirred for 2 h. This solution at 0°C was transferred via cannulation to the other flask containing the malonate anion solution. After stirring at rt for 2 days, without workup the reaction mixture was purified by flash chromatography eluting with 5% to 20% diethyl ether in petroleum ether to afford **5b** (48 mg, 0.18 mmol, 79%) as a colorless oil.

IR (film) cm^{-1}: 3006w, 2954m, 2925m, 2855w, 1740s, 1654w, 1560w, 1437m, 1292m, 1212s, 1072m, 932w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.13 (m, 1H), 4.90 (m, 1H), 3.75 (s, 6H), 2.95 (dd, J=1.0, 8.0 Hz, 2H), 2.79 (d, J=2.5 Hz, 2H), 1.76 (s, 3H), 1.67 (m, 1H), 0.75 (m, 2H), 0.35 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.7, 138.9, 120.1, 78.6, 73.5, 57.4, 52.7, 30.2, 29.7, 22.9, 7.01, 6.60, 3.47; HRMS (EI+) Calc'd for $C_{15}H_{20}O_4$ (M^+): 262.1362. Found: 262.1364.

5c:



5c



5c

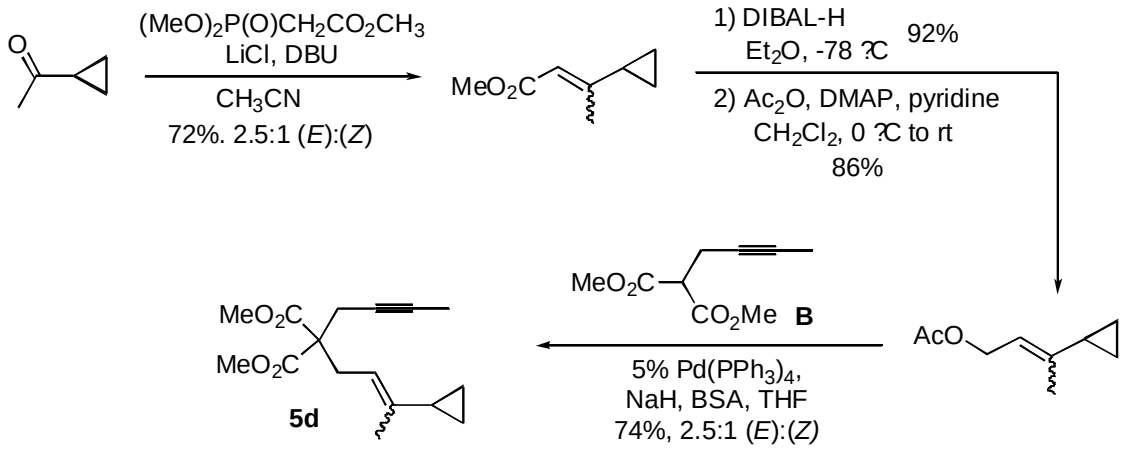
4,4-Bis(methoxycarbonyl)-7-cyclopropyl-1-phenyl-hept-6(*E*)-en-1-yne (**5c**): To a degassed flask containing Pd_2dba_3•$CHCl_3$ (40 mg, 0.039 mmol) and triphenylphosphine (60 mg, 0.229 mmol) was added THF (3 mL). After stirring at rt for 10 min, to the resulting orange solution was added a solution of 3-phenyl-2-propynyl diethyl malonate[13] (200 mg, 0.813 mmol) and methyl (1-cyclopropylpro-2-en-1-yl)carbonate[14] (130 mg, 0.833 mmol) in THF (3 mL). After an additional 12 h at rt, the solution was concentrated *in vacuo* and chromatographed eluting with 10:1 petroleum ether:diethyl ether to afford **5c** (188 mg, 71%) as a colorless liquid.

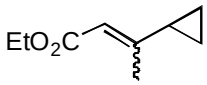
[13] a. Son, S.U.; Park, K.H.; Chung, Y.K. *J. Am. Chem. Soc.* **2002**, *124*, 6838. b. Hicks, F.A.; Kablaoui, N.M.; Buchwald, S.L.; *J. Am. Chem. Soc.* **1999**, *121*, 5881.

[14] For preparation of this compound, see preparation of **5a**, above.

IR (film): 3081, 3004, 2953, 2842, 1738, 1491, 1436, 1328, 1291, 1269, 1212, 1070, 1028, 966, 758, 692 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.38 (m, 2H), 7.29 (m, 2H), 5.36 (dt, *J* = 15.2 and 7.5 Hz, 1H), 5.15 (dd, *J* = 15.2 and 8.8 Hz, 1H), 3.77 (s, 6H), 3.03 (s, 2H), 2.81 (d, *J* = 7.5 Hz, 2H), 1.37 (m, 1H), 0.69 (m, 2H), 0.34 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.4, 139.6, 131.6, 128.2, 127.9, 123.2, 120.2, 84.4, 83.4, 57.5, 52.7, 35.4, 23.5, 13.6, 6.6; HRMS (EI+) Calc'd for $C_{20}H_{22}O_4$: 326.1518. Found: 326.1519.

5d:

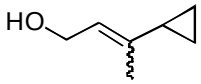




3-Cyclopropyl-but-2-enoic acid ethyl ester: To a solution of triethyl phosphonoacetate (340 mg, 1.52 mmol) in dry acetonitrile (5 mL) was added lithium chloride (120 mg, 2.84 mmol) followed by DBU (0.34 mL, 2.18 mmol). To the resulting yellow solution was slowly added a solution of 1-bycloproyl-ethanone (150 mg, 1.79 mmol) in acetonitrile (5 mL). After stirring at rt for 8 h, the reaction mixture was diluted with diethyl ether (30 mL), washed with 1N sodium bisulfate (2 x 25 mL), brine (25 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 10:1 petroleum ether:diethyl ether afforded a 2.5:1 mixture of *E*:*Z* olefins (184 mg, 72%) as a colorless liquid. The ratio of (*E*):(*Z*)-olefins was determined using ^{1}H-NMR by integration of one of the olefinic protons: a singlet at 5.63 ppm for the (*Z*)-olefin and a singlet at 5.59 ppm the (*E*)-olefin.

IR (film): 3091, 3012, 2950, 1715, 1630, 1447, 1253, 1194, 1159, 1112, 1076, 1032, 911, 843 cm^{-1}. (*E*)-isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.59 (s, 1H), 4.02 (q, *J* = 7.0 Hz, 2H), 1.90 (s, 3H), 1.46 (m, 1H), 1.18 (t, *J* = 7.0 Hz, 3H), 0.70 (m, 2H), 0.60 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 166.5, 161.2, 113.2, 59.1, 19.9, 14.9, 14.2, 6.6.

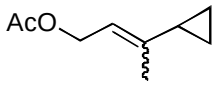
Additional signals for the (Z)-isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.63 (s, 1H), 4.04 (q, *J* = 7.0 Hz, 2H), 3.15 (m, 1H), 1.44 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H), 0.78 (m, 2H), 0.68 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 166.9, 160.5, 116.1, 61.4, 18.4, 13.9, 13.7, 6.5.



3-Cyclopropyl-but-2-en-1-ol: To a solution of the α,β-unsaturated esters (180 mg, 1.07 mmol) in methylene chloride (5 mL), at -78 ºC, was added 1.0 M di-*iso*-butylaluminum hydride (3 mL, 3.00 mmol). After stirring at -78 ºC 8 h, the solution was quenched ethyl acetate (0.5 mL), followed by saturated potassium sodium tartrate (5 mL). After stirring at rt 2 h, the biphasic solution was separated and the aqueous layer extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried ($MgSO_4$), concentrated *in vacuo*, and chromatographed eluting with 40% diethyl ether:petroleum ether to afford a 2.2:1 mixture of *E*:*Z*-allylic alcohols (110 mg, 92%) as a colorless liquid. The ratio of (*E*):(*Z*)-allylic alcohols was determined using ^{1}H-NMR by integration of one of the olefinic protons: a triplet at 5.48 ppm for the (*Z*)-olefin and a triplet at 5.35 ppm the (*E*)-olefin.

IR (film): 3333, 3083, 3007, 2919, 2872, 1660, 1428, 1386, 1240, 1000, 895, 816 cm^{-1}. *E*-isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.35 (t, *J* = 6.8 Hz, 1H), 4.04 (d, *J* = 6.8 Hz, 2H), 2.38 (br s, 1H), 1.47 (s, 3H), 1.31 (m, 1H), 0.50 (m, 2H), 0.39 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 139.7, 121.7, 58.8, 18.5, 13.7, 4.4.

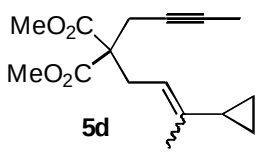
Additonal signals for the *Z*-isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.48 (t, *J* = 7.0 Hz, 1H), 4.27 (d, *J* = 7.0 Hz, 2H), 1.90 (br s, 1H), 1.69 (m, 1H), 1.44 (s, 3H), 0.64 (m, 2H), 0.56 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 139.4, 124.5, 58.6, 18.6, 12.3, 4.3.



3-Cyclopropylbuten-2-en-1-ylacetate:[15] To a solution of the allylic alcohols (110 mg, 0.982 mmol) and 4-*N*,*N*-dimethylpyridine (5 mg, 0.041 mmol) in methylene chloride (10 mL), at 0 ºC, was added pyridine (0.12 mL, 1.48 mmol) followed by acetic anhydride 0.12 mL, 0.13 mmol). After stirring at rt for 8h, the solution was washed with 1N hydrochloric acid (5 mL), saturated sodium bicarbonate (5 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 3:1 petroleum ether: diethyl ether afforded a 2.2:1 mixture of (*E*:*Z*)-3-cyclopropylbuten-2-en-1-ylacetate (130 mg, 86%) as a colorless liquid. The (*E*):(*Z*)-ratio was determined using ^{1}H-NMR by integration of one of the allylic methine protons: a doublet at 4.64 ppm for (*Z*)-3-cyclopropylbuten-2-en-1-ylacetate and a doublet at 4.49 ppm (*E*)-3-cyclopropylbuten-2-en-1-ylacetate.

IR (film): 3088, 3010, 1738, 1652, 1446, 1376, 1229, 1022, 950 cm^{-1}. *E*-isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.30 (t, *J* = 7.1 Hz, 1H), 4.49 (d, *J* = 7.1 Hz, 2H), 1.96 (s, 3H), 1.49 (s, 3H), 1.33 (m, 1H), 0.52 (m, 2H), 0.41 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 171.1, 143.1, 116.5, 61.2, 21.0, 18.7, 13.8, 4.7.

Additonal signals for the *Z*-isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.33 (t, *J* = 7.3 Hz, 1H), 4.64 (d, *J* = 7.3 Hz, 2H), 1.98 (s, 3H), 1.62 (m, 1H), 1.39 (s, 3H), 0.59 (m, 2H), 0.49 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 171.1, 142.4, 119.3, 60.9, 21.1, 18.9, 12.4, 4.5.



5d

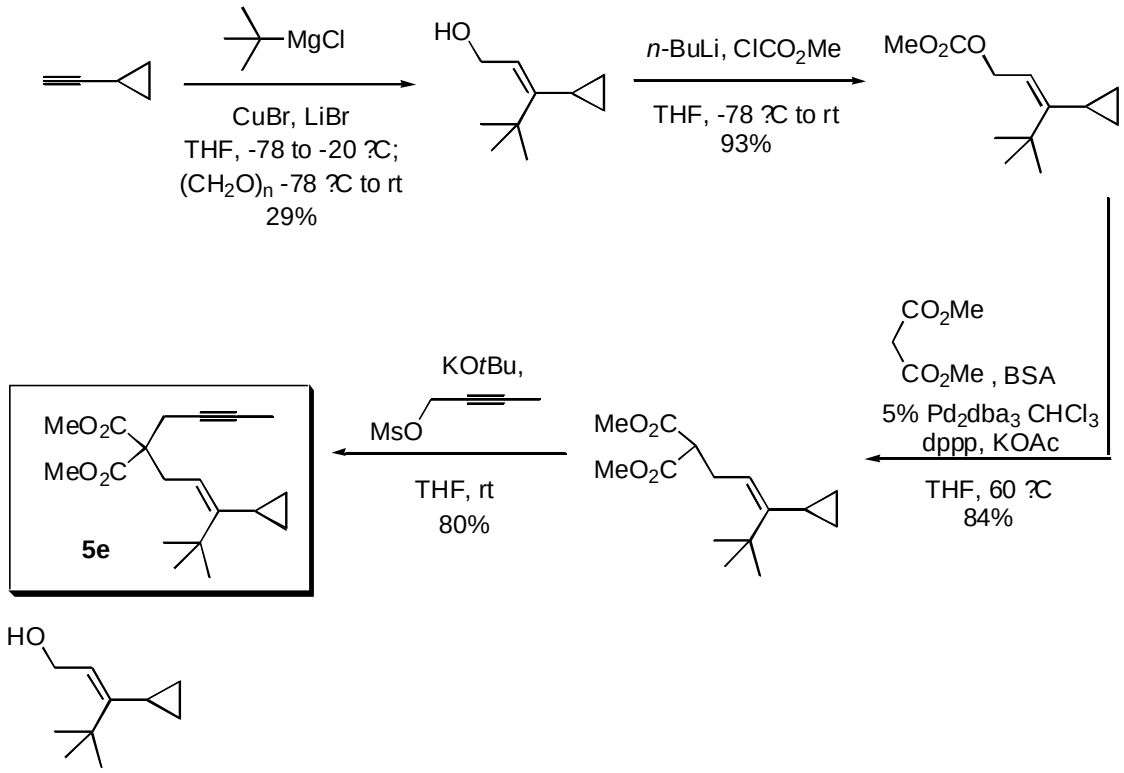
[15] Balbler, J.H.; Coghlan, M.J.; Giacherio, D.J. *J. Org. Chem.* **1977**, *42*, 2172.

5,5-Bis(methoxycarbonyl)-8-cyclopropyl-non-7(*E*)-en-2-yne (5d):[16] To a solution of alkyne **A**[16] (200 mg, 1.09 mmol), tetrakis(triphenylphosphine) palladium(0) (63 mg, 0.055 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (0.56 mL, 0.217 mmol) and 60% sodium hydride (52 mg, 1.3 mmol) in THF (1 mL) was added a solution of (*E*)- and (*Z*)-3-cyclopropylbuten-2-en-1-ylacetates (180 mg, 1.17 mmol) in THF (1 mL). After stirring at rt for 8 h, the solution was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate, dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 8:1 petroleum ether:diethyl ether afforded **5d** (214 mg, 74% yield) as a 2.5:1 mixture of *E*:*Z* olefin isomers. The ratio of olefin isomers was determined by integration of the ^{1}H-NMR signal for the vinyl methyl group: a singlet at 1.53 ppm for the *E*-isomer and a singlet at 1.39 ppm for the *Z*-isomer.

IR (film): 3283, 3002, 2954, 1739, 1437, 1291, 1206, 1054 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.98 (t, *J* = 7.8 Hz, 1H), 3.72 (s, 6H), 2.78 (d, *J* = 7.8 Hz, 2H), 2.71 (q, *J* = 2.5 Hz, 2H), 1.75 (t, *J* = 2.5 Hz, 3H), 1.53 (s, 3H), 1.36 (ddd, *J* = 13.6, 5.3 and 3.1 Hz, 1H), 0.55 (m, 2H), 0.41 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.7, 140.6, 115.5, 78.6, 73.6, 57.4, 52.5, 30.4, 22.7, 19.0 13.6, 4.5, 3.4.

Additional signals for the *Z*-isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.01 (t, *J* = 7.5 Hz, 1H), 3.73 (s, 6H), 2.93 (d, *J* = 7.5 Hz, 2H), 2.76 (q, *J* = 2.5 Hz, 2H), 1.39 (s, 3H).

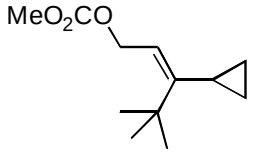
5e:



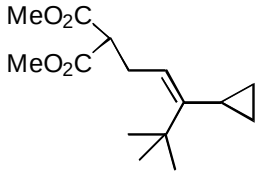
3-Cyclopropyl-4,4-dimethyl-pent-2(*Z*)-en-1-ol: Copper(I) bromide (4.3 g, 30 mmol) and LiBr (2.6 g, 30 mmol) were dried for 1 h *in vacuo*. THF (120 mL) was added and the suspension cooled to -78 °C. *t*-Butyl magnesium chloride (30 mL, 2M in Et_2O, 60 mmol) was added

[16] For preparation of this compound, see preparation of **5b**, above.

dropwise and the white suspension warmed to -60 °C and stirred 2 h. Ethynyl-cyclopropane (2.4 mL, 28.5 mmol) was added at -50 °C and the mixture stirred for 1 h between -20 and -30 °C. The reaction was cooled to -78 °C and paraformaldehyde (2.7 g. 90 mmol) was added. The mixture was then allowed to warm to rt and stirred an additional 16 h. A solution of 50 mL saturated aqueous NH_4Cl and 30 mL 10% aqueous HCl was added dropwise at 0 °C and the aqueous phase was extracted with Et_2O (4 x 80 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (gradient elution 6:1 to 2:1 petroleum ether:diethyl ether) to afford 3-cyclopropyl-4,4-dimethyl-pent-2(*Z*)-en-1-ol (1.16 g, 8.27 mmol, 29% yield) as a colorless oil.
R_f = 0.14 (PE/Et_2O = 3:1; anisaldehyde); IR (film): 3334, 3082, 2956, 2870, 1642, 1479, 1426, 1395, 1363, 1202, 1039, 1020, 986 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.13 (t, J=6.3 Hz, 1H), 4.27 (d, J=6.3 Hz, 2H), 1.35 (m, 1H), 1.13 (s, 9H), 0.55 (m, 2H), 0.34 (m, 2H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 149.1, 124.0, 60.1, 31.7, 30.6, 17.1, 5.9. Anal. Calc'd for $C_{10}H_{18}O$; C, 77.87; H, 11.76. Found: C, 78.06; H, 11.58.

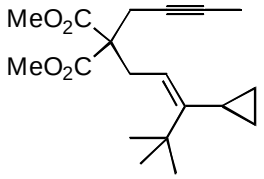


Carbonic acid 3-cyclopropyl-4,4-dimethyl-pent-2(*Z*)-enyl ester methyl ester: 3-Cyclopropyl-4,4-dimethyl-pent-2(*Z*)-en-1-ol (1.16 g, 7.53 mmol) was dissolved in 50 mL THF, cooled to -78 °C, and treated with *n*-BuLi (5.1 mL, 1.55 M in hexanes, 7.9 mmol). The solution was stirred for 10 min, then methylchloroformate (0.87 mL, 11.3 mmol) was added and the reaction mixture was allowed to warm to ambient temperature over a period of 3 h. The solution was diluted with 50 mL Et_2O and quenched with 30 mL of water. The aqueous phase was extracted with Et_2O (3 x 50 mL), the combined organic phases dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (gradient elution 100:1 to 5:1 petroleum ether:diethyl ether) to afford carbonic acid 3-cyclopropyl-4,4-dimethyl-pent-2(*Z*)-enyl ester methyl ester (1.49 g, 7.01 mmol, 93% yield) as a colorless oil.
R_f = 0.63 (PE/Et_2O = 3:1; anisaldehyde); IR (film): 2958, 1750, 1443, 1365, 1268, 956, 793 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.11 (t, J=6.3 Hz, 1H), 4.82 (d, J=6.3 Hz, 2H), 3.74 (s, 3H), 1.37 (m, 1H), 1.18 (s, 9H), 0.57 (m, 2H), 0.35 (m, 2H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 155.7, 152.0, 117.8, 65.7, 54.6, 31.4, 30.6, 17.3, 6.1. Anal. Calc'd for $C_{12}H_{20}O_3$; C, 67.89; H, 9.50. Found: C, 68.06; H, 9.68.



2-(3-Cyclopropyl-4,4-dimethyl-pent-2(*Z*)-enyl)-malonic acid dimethyl ester: Carbonic acid 3-cyclopropyl-4,4-dimethyl-pent-2(*Z*)-enyl ester methyl ester (244 mg, 1.15 mmol), dimethylmalonate (304 mg, 2.3 mmol), $Pd_2(dba)_3$•$CHCl_3$ (60 mg, 0.058 mmol), dppp (48 mg, 0.12 mmol), KOAc (20 mg, 0.23 mmol), and BSA (50 mg, 1.72 mmol) were dissolved in 10 mL THF and heated at 60 °C in a sealed tube 16 h. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography (gradient elution 10:1 to 6:1 petroleum

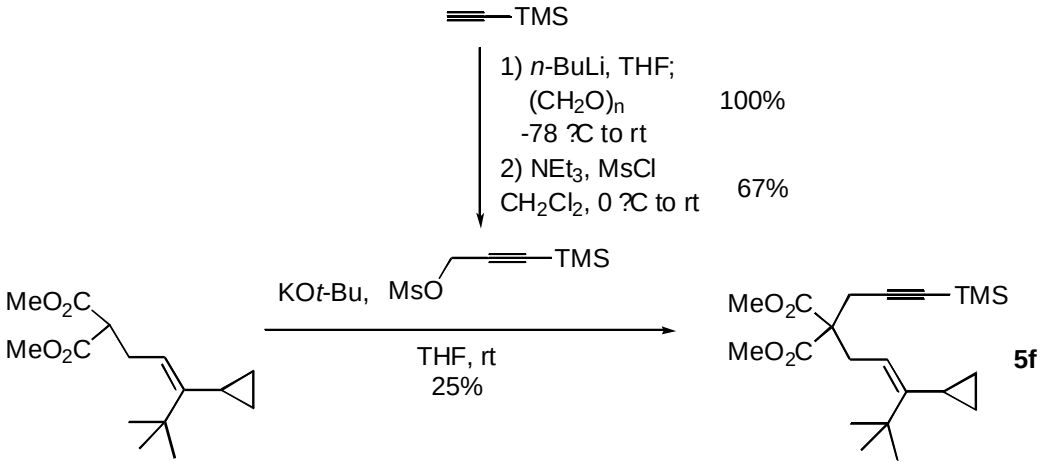
ether:diethyl ether) to afford 2-(3-cyclopropyl-4,4-dimethyl-pent-2(*Z*)-enyl)-malonic acid dimethyl ester (258 mg, 0.96 mmol, 84% yield) as a colorless liquid.
R_f = 0.45 (PE/Et_2O = 3:1; anisaldehyde); IR (film): 2955, 1739, 1436, 1340, 1274, 1230, 1203, 1154, 1023, 838 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.88 (t, J=7.5 Hz, 1H), 3.69 (s, 6H), 3.32 (t, J=7.5 Hz, 1H), 2.77 (t, J=7.5 Hz, 2H), 1.33 (m, 1H), 1.18 (s, 9H), 0.52 (m, 2H), 0.25 (m, 2H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 169.5, 150.0, 119.5, 52.4, 52.3, 35.9, 30.5, 28.6, 17.6, 5.9. Anal. Calc'd for $C_{15}H_{24}O_4$; C, 67.14; H, 9.01. Found: C, 67.28; H, 8.88.

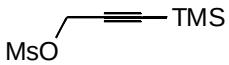


5e

2-But-2-ynyl-2-(3-cyclopropyl-4,4-dimethyl-pent-2(*Z*)-enyl)-malonic acid dimethyl ester (**5e**): 2-(3-Cyclopropyl-4,4-dimethyl-pent-2(*Z*)-enyl)-malonic acid dimethyl ester (263 mg, 0.98 mmol) was dissolved in 10 mL THF and treated with *t*-BuOK (165, 1.47 mmol). The solution was stirred for 15 min at rt and methanesulfonic acid but-2-ynyl ester (336, 1.67 mmol) was added dropwise. The mixture was stirred for 3 h then poured into brine. The aqueous solution was extracted with Et_2O (3 x 20 mL), the combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo.* Flash chromatography eluting with 9:1 petroleum ether:diethyl ether afforded **5e** (252 mg, 0.79mmol, 80% yield) as a colorless oil.
R_f = 0.47 (PE/Et_2O = 3:1; anisaldehyde); IR (film): 3080, 2954, 2870, 1740, 1436, 1363, 1327, 1292, 1203, 1055, 950, 882 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.78 (t, *J*=6.0 Hz, 1H), 3.68 (s, 6H), 2.92 (d, *J*=6.0 Hz, 2H), 2.70 (q, *J*=2.7 Hz, 2H), 1.70 (t, *J*=2.7 Hz, 3 H), 1.34 (m, 1H), 1.20 (s, 9H), 0.52 (m, 2H), 0.25 (m, 2H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 170.7, 150.7, 117.0, 78.8, 73.5, 57.5, 54.7, 52.5, 31.4, 30.5, 22.9, 17.9, 5.9, 3.4. Anal. Calc'd for $C_{19}H_{28}O_4$; C, 71.22; H, 8.81. Found: C, 71.33; H, 8.67.

5f:

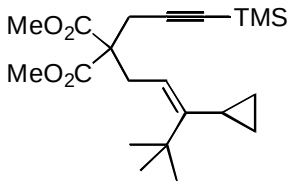




Methanesulfonic acid 3-trimethylsilanyl-prop-2-ynyl ester: Trimethylsilylacetylene (4.23 mL, 2.94 g, 30 mmol) was dissolved in 120 mL THF, cooled to -78 °C, and treated with *n*-BuLi (3.6 mL, 10.0 M hexanes, 36 mmol). The solution was stirred for 30 min and paraformaldehyde (1.8 g, 60 mmol) was added and the reaction allowed to warm to rt. After 12 h, the reaction was cooled to 0 °C and quenched by addition of 50 mL 10% aqueous HCl. The solution was diluted with Et_2O and extracted. The organic phase was washed with saturated aqueous Na_2CO_3 and the aqueous phases were each reextracted with 20 mL Et_2O. The combined organic phases were dried over $MgSO_4$ and the solvent concentrated *in vacuo.* 3-Trimethylsilyl-2-propyn-1-ol was obtained as a colorless oil in 100% yield (3.84 g, 30 mmol).
^{1}H-NMR (300 MHz, $CDCl_3$): 4.25 (s, 2H), 0.16 (s, 9H). The spectroscopic data agreed with ref.[17]

3-Trimethylsilyl-2-propyn-1-ol (2.21 g, 17.3 mmol) and triethylamine (3.0 mL, 2.26 g, 24.1 mmol) were dissolved in 40 mL CH_2Cl_2 and cooled to 0 °C. The reaction was treated with mesityl chloride (1.47 mL, 2.17g, 19.0 mmol), then allowed to warm to rt over 4 h then poured into 30 mL 10% aqueous HCl. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic phases were washed with brine then dried over $MgSO_4$. The solvent was concentrated *in vacuo* and the residue purified by flash chromatography eluting with 2:1 petroleum ether:diethyl ether to afford methanesulfonic acid 3-trimethylsilanyl-prop-2-ynyl ester (2.41 g, 11.6 mmol, 67% yield) as a colorless oil.
^{1}H-NMR (300 MHz, $CDCl_3$): 4.82 (s, 2H), 3.11 (s, 3H), 0.18 (s, 9H). The spectroscopic data agreed with ref.[18]

[17] a. Jones, T.K.; Denmark, S.E. *Org. Syn.* **1985**, *64*, 182. b. Harris, N.J.; Gajewski, J.J. *J. Am. Chem. Soc.* **1994**, *116*, 6121-6129.
[18] Ma, C.; Liu, X.; Yu, S.; Zhao, S.; Cook, J.M. *Tetrahedron Lett.* **1999**, *40*, 657-660.

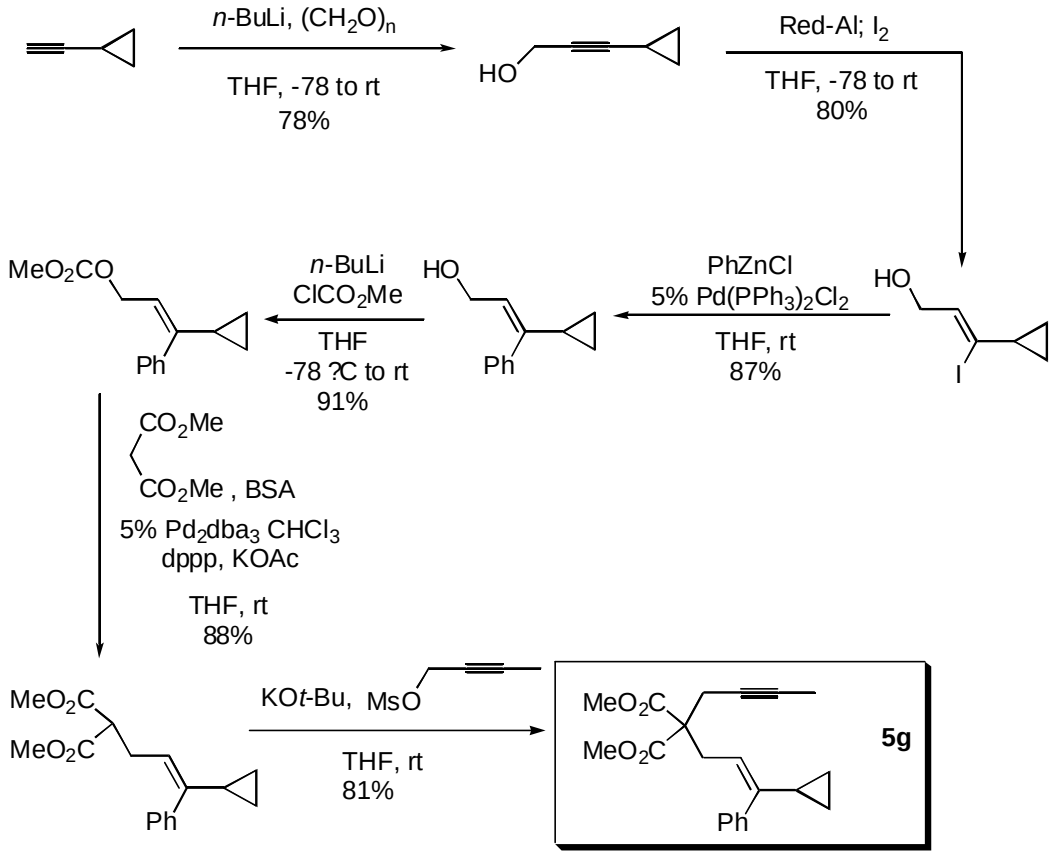


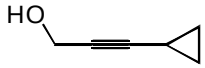
5f

2-(3-Cyclopropyl-4,4-dimethyl-pent-2-enyl)-2-(3-trimethylsilanyl-prop-2-ynyl)-malonic acid dimethyl ester (**5f**): 2-(3-Cyclopropyl-4,4-dimethyl-pent-2(*Z*)-enyl)-malonic acid dimethyl ester (342 mg, 1.28 mmol) in 12 mL THF was treated with 200 mg *t*-BuOK (200 mg, 1.78 mmol) at 0 °C and the reaction stirred 10 min. Methanesulfonic acid 3-trimethylsilanyl-prop-2-ynyl ester (423 mg, 2.04 mmol) was added and the solution stirred 1 h at rt. The reaction was poured into 20 mL of water, the aqueous phase extracted with Et_2O (3 x 20 mL), the combined organic layers dried over $MgSO_4$, and the solvent concentrated *in vacuo*. The residue was purified by flash chromatography eluting with 9:1 petroleum ether:diethyl ether to afford **5f** (245 mg, 0.65 mmol, 51% yield) as a colorless oil.

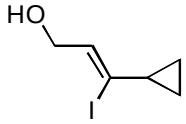
R_f = 0.55 (PE/Et_2O = 3:1; anisaldehyde); IR (film): 2956, 2180, 1741, 1436, 1292, 1251, 1217, 1027, 845, 761 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.74 (t, J=7.2 Hz, 1H), 3.70 (s, 6H), 2.94 (d, J=7.2 Hz, 2H), 2.77 (s, 2H), 1.35 (m, 1H), 1.22 (s, 9H), 0.53 (m, 2H), 0.25 (m, 2H), 0.09 (s, 9H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 170.4, 151.0, 116.9, 101.4, 88.0, 57.4, 52.5, 36.0, 31.3, 30.6, 23.9, 17.9, 5.9, -0.1. Anal. Calc'd for $C_{21}H_{34}O_4Si$; C, 66.62; H, 9.05. Found: C, 66.74; H, 8.85.

5g:

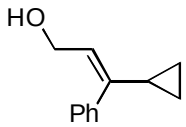




3-Cyclopropyl-prop-2-yn-1-ol:[19] To a solution of cyclopropylacetylene (5.0 g, 75.8 mmol) in diethyl ether (100 mL), at -78 ºC, was added *n*-BuLi (50 mL, 1.5 M in hexanes, 75 mmol) resulting in the formation of a thick white suspension which was warmed to room temperature over 1 h. To the suspension was added paraformaldehyde (4.5g, 152 mmol) and stirring continued at room temperature for 4 h. The white suspension was quenched with 1N sodium bisulfate (200 mL) and the biphasic solution separated and the aqueous layer extracted with diethyl ether (2 x 100 mL). The combined diethyl ether extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Kugelrohr distillation afforded 3-cyclopropyl-prop-2-yn-1-ol (5.70 g, 78%) as a colorless liquid.
IR (film): 3383, 3095, 3012, 2902, 2869, 2252, 1428, 1361, 1110, 1044, 877, 814 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.16 (s, 2H), 2.15 (br s, 1H), 1.20 (m, 1H), 0.73 (m, 2H), 0.64 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 87.7, 73.6, 51.2, 8.1, -0.7.



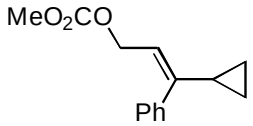
3-Cyclopropyl-3-iodo-prop-2(*Z*)-en-1-ol: To a solution of 3-cyclopropyl-prop-2-yn-1-ol[19] (2.4 g, 25.0 mmol) in THF (100 mL), at -78 ºC, was slowly added Red-Al (8.3 mL, 65 wt%, 27.5 mmol) and the solution allowed to warm to room temperature. After an additional 10 h, the clear yellow solution was recooled to -78 ºC and treated with iodine (8.0 g, 30.0 mmol). After 30 min. at -30 ºC, the solution was warmed to room temperature, quenched with saturated sodium thiosulfate (150 mL) and the biphasic solution separated. The organic layer was dried ($MgSO_4$), concentrated *in vacuo*, and chromatographed eluting with 1:1 petroleum ether:diethyl ether to afford 3-cyclopropyl-3-iodo-prop-2(*Z*)-en-1-ol (5.09 g, 91 %) as a colorless oil.
IR (film): 3330, 3084, 3006, 2869, 1635. 1455, 1423, 1357, 1194, 1147, 1076, 1023, 985, 849, 820 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.87 (td, *J* = 5.7 and 1.3 Hz, 1H), 4.15 (t, *J* = 5.7 Hz, 2H), 2.09 (br s, 1H), 1.62 (m, 1H), 0.73 (m, 2H), 0.65 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 131.8, 113.3, 67.0, 24.3, 8.9. Anal. Calc'd for C_6H_9IO; C, 32.17; H, 4.05. Found: C, 32.35; H, 4.18.



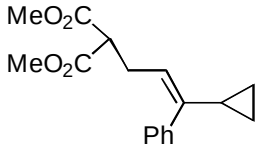
3-Cyclopropyl-3-phenyl-prop-2(*Z*)-en-1-ol: $ZnCl_2$ (4.6 g, 33.5 mmol) was dried under vacuum, then dissolved in 60 mL THF. The solution was treated dropwise at rt with C_6H_5MgCl (13.4 mL, 2M in THF, 26.8 mmol). The resulting white suspension was stirred 2 h then solid $Pd(PPh_3)Cl_2$ (235 mg, 0.34 mmol) was added. After 10 min a solution of 3-cyclopropyl-3-iodo-prop-2(*Z*)-en-1-ol (1.5 g, 6.7 mmol) in 5 mL THF was added. The resulting mixture was stirred for 3 h. The reaction mixture was poured into 50 mL water and the aqueous phase was extracted with Et_2O (5 x 50 mL). The combined organic layers were dried over $MgSO_4$, concentrated *in vacuo*, and

[19] Shvrin, K.N.; Krylova, I.V.; Shredova, I.B.; Okonnoshnikova, G.P.; Dolgii, I.E.; Nefedov, D.M. *J. Chem. Soc., Perkin Trans. 2* **1991**, *12*, 1875.

purified by flash chromatography (gradient elution 3:1 to 2:1 petroleum ether:diethyl ether) to afford 3-cyclopropyl-3-phenyl-prop-2(*Z*)-en-1-ol (1.014 g, 5.82 mmol, 87% yield) as a slightly reddish oil.
R_f = 0.13 (PE/Et_2O = 3:1; anisaldehyde); IR (film): 3333, 3081, 3008, 1648, 1493, 1442, 1023, 986, 766, 702 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.28 (m, 3H), 7.14 (m, 2H), 5.63 (t, J=7.2 Hz, 1H), 3.96 (dd, J=7.2, 66 Hz, 2H), 1.13 (m, 1H), 0.68 (m, 2H), 0.47 (m, 2H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 145.4, 139.1, 128.4, 127.9, 127.0, 123.6, 60.0, 18.1, 5.6. Anal. Calc'd for $C_{10}H_{18}O$; C, 82.72; H, 8.10. Found: C, 82.60; H, 7.91.



Carbonic acid 3-cyclopropyl-3-phenyl-allyl ester methyl ester: 3-Cyclopropyl-3-phenyl-prop-2(*Z*)-en-1-ol (880 mg, 5.06 mmol) was dissolved in 40 mL THF and treated with *n*-BuLi (3.9 mL, 1.55 mL in hexanes, 6.06 mmol) at -78 °C. The solution was stirred for 10 min, then methylchloroformate (0.59 mL, 7.58 mmol) was added and the reaction mixture was allowed to warm to rt over a period of 3 h. The solution was diluted with 20 mL Et_2O and quenched with 40 mL of water. The aqueous phase was extracted with Et_2O (3 x 30 mL), the combined organic phases dried over $MgSO_4$, and concentrated *in vacuo.* The residue was purified by flash chromatography eluting with 8:1 petroleum ether:diethyl ether to afford carbonic acid 3-cyclopropyl-3-phenyl-allyl ester methyl ester (1.07 g, 4.61 mmol, 91% yield) as a colorless oil.
R_f = 0.49 (PE/Et_2O = 3:1; anisaldehyde); IR (film): 3008, 2958, 2861, 1748, 1443, 1373, 1264, 1023, 942, 793, 768, 704 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.30 (m, 3H), 7.14 (m, 2H), 5.61 (t, J=7.2 Hz, 1H), 4.46 (d, J=7.2 Hz, 2H), 3.74 (s, 3H), 1.28 (m, 1H), 0.70 (m, 2H), 0.49 (m, 2H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 155.7, 149.1, 138.3, 128.5, 128.0, 127.4, 117.9, 65.6, 54.6, 39.0, 25.7, 23.3. Anal. Calc'd for $C_{14}H_{16}O_3$; C, 72.39; H, 6.94. Found: C, 71.95; H, 7.95.



2-(3-Cyclopropyl-3-phenyl-allyl)-malonic acid dimethyl ester: Carbonic acid 3-cyclopropyl-3-phenyl-allyl ester methyl ester (242 mg, 1.04 mmol), dimethylmalonate (275 mg, 2.08 mmol), $Pd_2(dba)_3$•$CHCl_3$ (54 mg, 0.052 mmol), dppp (43 mg, 0.104 mmol), KOAc (20 mg, 0.23 mmol), and BSA (317 mg, 1.56 mmol) were dissolved in 10 mL THF and stirred for 16 h at rt. The solvent was removed *in vacuo* and the residue purified by flash chromatography (gradient elution 10:1 to 6:1 petroleum ether:diethyl ether) to afford 2-(3-cyclopropyl-3-phenyl-allyl)-malonic acid dimethyl ester (264 mg, 0.92 mmol, 88% yield) as a colorless oil.
R_f = 0.42 (PE/Et_2O = 3:1; anisaldehyde); IR (film): 3006, 2954, 1737, 1437, 1340, 1276, 1228, 1156, 1025, 767, 704 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.27 (m, 3H), 7.09 (d, J=6.6 Hz, 2H), 5.35 (t, J=7.5 Hz, 1H), 3.67 (s, 6H), 3.31 (t, J=7.5 Hz, 1H), 2.47 (t, J=7.5 Hz, 2H), 1.55 (m, 1H), 0.62 (m, 2H), 0.35 (m, 2H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 169.3, 145.3, 139.1, 128.6, 127.9, 126.8, 119.9, 52.3, 51.8, 42.0, 28.1, 5.2. Anal. Calc'd for $C_{17}H_{20}O_4$; C, 70.81; H, 6.99. Found: C, 70.68; H, 7.68

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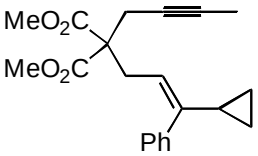
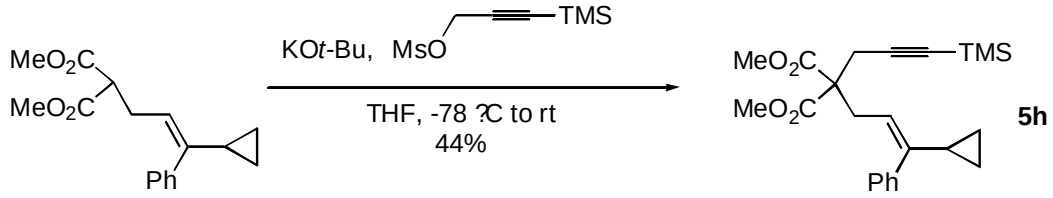


5g

2-But-2-ynyl-2-(3-cyclopropyl-3-phenyl-allyl)-malonic acid dimethyl ester (**5g**): 2-(3-cyclopropyl-3-phenyl-allyl)-malonic acid dimethyl ester (228 mg, 0.79 mmol) was dissolved in 8 mL THF and treated with KO*t*-Bu (132 mg, 1.18 mmol). The solution was stirred 15 min at rt and methanesulfonic acid but-2-ynyl ester[Fehler! Textmarke nicht definiert.] (271 mg, 1.34 mmol) was added dropwise. The mixture was stirred 3 h, then poured into brine. The aqueous solution was extracted with Et_2O (3 x 20 mL), the combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography eluting with 9:1 petroleum ether:diethyl ether to afford **5g** (218 mg, 0.64 mmol, 81% yield) as a colorless oil.
R_f = 0.50 (PE/Et_2O = 3:1; anisaldehyde); IR (film): 3005, 2954, 2361, 1738, 1493, 1438, 1292, 1210, 1072, 767, 704 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.25 (m, 3H), 7.08 (d, J=6.6 Hz, 2H), 5.20 (t, J=7.5 Hz, 1H), 3.64 (s, 6H), 2.66 (q, J=2.4 Hz, 2H), 2.63 (d, J=7.5 Hz, 2H), 1.58 (t, J=2.4 Hz, 3H), 1.52 (m, 1H), 0.59 (m, 2H), 0.36 (m, 2H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 170.6, 146.4, 139.1, 128.9, 127.7, 126.7, 117.9, 78.7, 73.2, 57.3, 52.8, 52.5, 22.9, 18.8, 5.3, 3.4. Anal. Calc'd for $C_{21}H_{24}O_4$; C, 74.09; H, 7.11. Found: C, 74.11; H, 7.23.

5h:

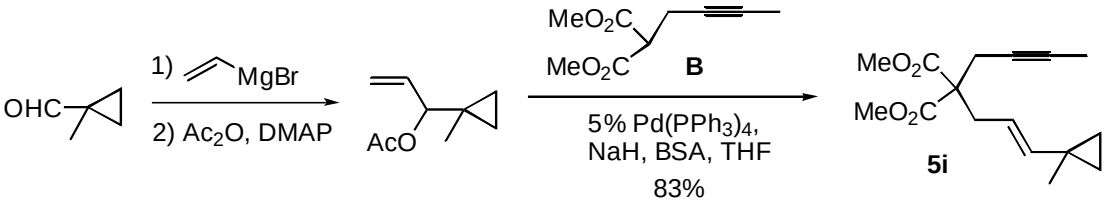


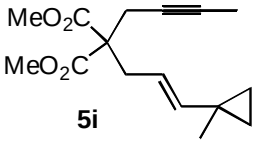
5h

2-(3-Cyclopropyl-3-phenyl-allyl)-2-(3-trimethylsilanyl-prop-2-ynyl)-malonic acid dimethyl ester (**5h**): 2-(3-cyclopropyl-3-phenyl-allyl)-malonic acid dimethyl ester (287 mg, 1.0 mmol) was dissolved in 10 mL THF and treated with KO*t*-Bu (157 mg, 1.4 mmol). The solution was stirred for 5 min at rt then cooled to -78 °C and methanesulfonic acid 3-trimethylsilanyl-prop-2-ynyl ester[17,18] (331 mg, 1.6 mmol) was added dropwise. The mixture was allowed to warm to rt over 2 h and stirred an additional 3 h. The solution was then poured into 20 mL 10% aqueous HCl, the aqueous solution extracted with Et_2O (3 x 20 mL), the combined organic phases dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography (gradient elution 8:1 to 5:1 petroleum ether:diethyl ether) to afford **5h** (174 mg, 0.44 mmol, 44% yield) as a colorless oil.
R_f = 0.43 (PE/Et_2O = 3:1; anisaldehyde); IR (film): 2955, 2180, 1739, 1437, 1291, 1251, 1208, 1025, 844, 761 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.27 (m, 3H), 7.08 (m, 2H), 5.22 (t, J=7.2 Hz, 1H), 3.64 (s, 6H), 2.74 (s, 2H), 2.63 (d, J=7.2 Hz, 2H), 1.25 (m, 1H), 0.60 (m, 2H), 0.35 (m, 2H), 0.03 (s, 9H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 170.3, 146.4, 139.1, 128.8, 127.9, 126.8, 117.8,

101.1, 87.8, 57.3, 52.5, 31.2, 24.1, 18.8, 5.3, -0.1. Anal. Calc'd for $C_{23}H_{30}O_4Si$; C, 69.31; H, 7.59. Found: C, 69.46; H, 7.36.

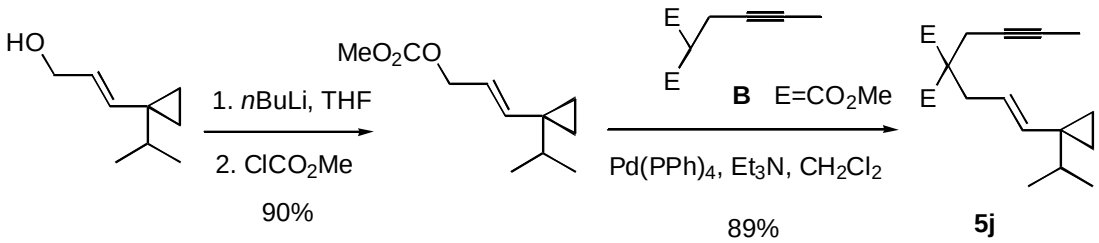
5i:



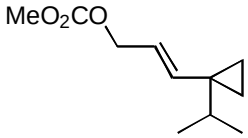


5,5-Bis(methoxycarbonyl)-8-(1-methylcycloprop-1-yl)-oct-7(*E*)-en-2-yne (**5i**): To a solution of alkyne **A** (100 mg, 0.543 mmol), tetrakis(triphenylphosphine) palladium(0) (31 mg, 0.027 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (0.28 mL, 0.109 mmol) and 60% sodium hydride (26 mg, 0.65 mmol) in THF (0.5 mL) was added a solution of acetic acid 1-(1-methyl-cyclopropyl)-allyl ester[20] (90 mg, 0.584 mmol) in THF (0.5 mL). After stirring at rt for 8h, the solution was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate, dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 8:1 petroleum ether: diethyl ether afforded **5i** (120 mg, 83% yield) as a colorless liquid.
IR (film): 2999, 2954, 1739, 1438, 1288, 1235, 1206, 1097, 970 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.21 (d, *J* = 15.3 Hz, 1H), 5.15 (dt, *J* = 15.3 and 6.8 Hz, 1H), 3.74 (s, 6H), 2.75 (q, *J* = 2.6 Hz, 2H), 2.74 (d, *J* = 6.8 Hz, 2H), 1.78 (t, *J* = 2.6 Hz, 3H), 1.14 (s, 3H), 0.54 (m, 2H), 0.52 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.6, 143.1, 118.4, 78.7, 73.4, 57.7, 52.5, 35.3, 22.9, 21.4, 17.1 14.9, 3.5; HRMS (EI+) Calc'd for $C_{16}H_{23}O_4$ (M + H^+): 279.1596. Found: 279.1602.

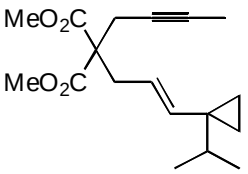
5j:



[20] Moiseenkov, A.M.; Ceskis, B.; Kudryavtseva, G.A.; Nesmeyanova, O.A.; Semenovskii, A.V. *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya* **1982**, *7*, 1572.



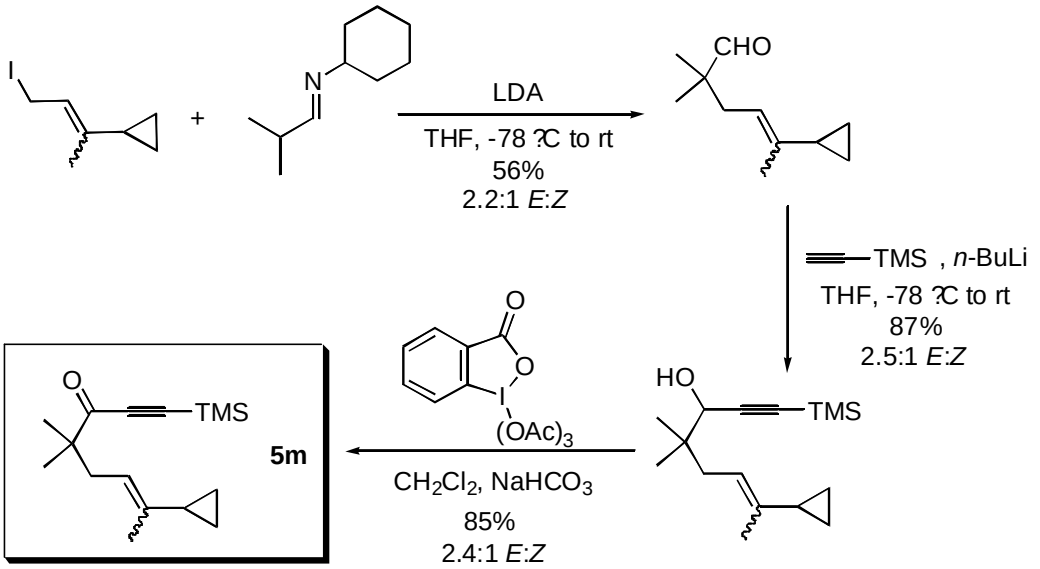
3-(1-Isopropyl-cyclopropyl)-allyl methyl carbonate: To a solution of 3-(1-isopropyl-cyclopropyl)-allyl alcohol (134 mg, 0.96 mmol) in 2 mL of distilled THF was added *n*-butyllithium (0.71 mL, 1.15 mmol, 1.6 M in hexane) at -78°C. After stirring at this temperature for 10 min, to this solution was added chloromethylformate (109 mg, 89 uL, 1.15 mmol). The mixture was slowly warmed to rt and stirred for additional 1 h. Without workup, the mixture was directly chromatographed eluting with 5% diethyl ether in petroleum ether to afford 3-(1-Isopropyl-cyclopropyl)-allyl methyl carbonate (171 mg, 0.86 mmol) as a colorless oil.
IR (neat): 2960s, 2875w, 1750s, 1444m, 1383w, 1266s, 1119w, 1067w, 972m, 946m, 793m cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.96 (d, *J*=15.3 Hz, 1H), 5.44 (dt, *J*=6.9, 15.3 Hz, 1H), 4.56 (dd, *J*=1.2, 6.9 Hz, 2H), 3.76 (s, 3H), 1.15 (m, 1H), 0.91 (d, *J*=6.6 Hz, 6H), 0.56 (m, 2H), 0.50 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 155.6, 138.9, 121.3, 88.8, 54.6, 34.9, 26.9, 25.4, 19.6, 13.2; HRMS (EI+) Calc'd for $C_9H_{15}O$ ($M-CO_2CH_3^+$): 139.1123. Found: 139.1126.

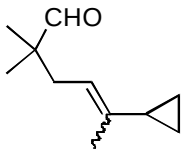


5j

Dimethyl 2-but-2-ynyl-2-[3-(1-isopropyl-cyclopropyl)-allyl]-malonate (**5j**): To a solution of malonate ester **A** (68 mg, 0.37 mmol) in 2 mL of dichloromethane was added triethyl amine (40 mg, 56 uL, 0.40 mmol) and palladium tetrakis(triphenylphosphine) (21 mg, 0.02 mmol). After dagassing with argon for 3 min, to the resulting dark orange solution was added a solution of 3-(1-isopropyl-cyclopropyl)-allyl methyl carbonate (80 mg, 0.40 mmol) in 0.5 mL of dichloromethane. The mixture as stirred at rt for an additional 2 h. Without workup, the reaction mixture was chromatographed eluting with 2-10% diethyl ether in petroleum ether to afford malonate **5j** (101 mg, 0.33 mmol, 89%) as a colorless oil.
IR (neat): 2958s, 1741s, 1438m, 1287m, 1207s, 1059w, 972w cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.76 (d, *J*=15.5 Hz, 1H), 5.14 (dt, *J*=8.0, 15.5 Hz, 1H), 3.74 (s, 6H), 2.72 (m, 4H), 1.78 (t, *J*=2.0 Hz, 3H), 1.06 (sep, *J*=7.0 Hz, 1H), 0.91 (d, *J*=7.0 Hz, 6H), 0.49 (m, 2H), 0.41 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.6, 136.7, 121.9, 78.7, 73.3, 57.5, 52.6, 35.4, 35.3, 27.3, 22.9, 19.7, 12.8, 3.48; HRMS (EI+) Calc'd for $C_{17}H_{23}O_4$ ($M-CH_3^+$): 291.1596. Found: 291.1580.

5m:



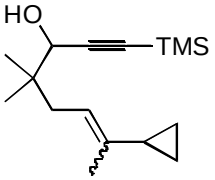


5-Cyclopropyl-2,2-dimethyl-hex-4(*E*)-en-1-al: To a solution of di-*iso*-propylamine (0.265 mL, 1.87 mmol) in THF (15 mL), at -78 ºC, was added *n*-BuLi (1.25 mL, 1.5 M in hexanes, 1.88 mmol). The solution was warmed to 0 ºC for 15 min., then recooled to -78 ºC. To the reaction mixture was slowly added a solution of cyclohexyl-isobutylidene-amine[21] (240 mg, 1.57 mmol). After stirring at -78 ºC for 2 h, the reaction mixture was treated with (3-iodo-1-methyl-propenyl)-cyclopropane (700 mg, 3.15 mmol), stirred at -78 ºC for 30 min. and then warmed to rt. After stirring at rt for 10 h, the reaction mixture was treated with 2N hydrochloric acid (50 mL) and stirred for an additional 10 h. The solution was diluted with diethyl ether (50 mL). The organic layer was separated, washed with 1N hydrochloric acid (2 x 25 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Kugelrohr distillation afforded 5-cyclopropyl-2,2-dimethyl-hex-4(*E*)-en-1-al (145 mg, 56 %) as a 2.2:1 mixture of *E*:*Z*-olefin isomers. The ratio of olefin isomers was determined by ^{1}H-NMR integration of the allylic methine protons: for the *E*-isomer a doublet at 2.19 ppm (2H) and for the *Z*-isomer a doublet at 2.26 ppm (2H).

IR (film): 3083, 2968, 2929, 2873, 2700, 1728, 1468, 1365, 1081, 887 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.48 (s, 1H), 5.14 (dq, *J* = 7.4 and 1.0 Hz, 1H), 2.19 (d, *J* = 7.4 Hz, 1H), 1.51 (s, 3H), 1.37 (m, 1H), 1.05 (d, *J* = 1.0 Hz, 6H), 0.54 (m, 2H), 0.42 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 207.1, 139.6, 117.8, 47.4, 36.1, 21.8, 19.7,14.8, 5.1; HRMS (EI+) Calc'd for $C_{11}H_{17}O$ ($M - H^+$): 165.1279. Found: 165.1280.

[21] a. Leboryne, J.F. *J. Organomet. Chem.* **1976**, *110*, 7255. b. De Kimpe, N.; Yao, Z.; De Buyck, L.; Verhe, R.; Schamp, N. *Bull. Soc. Chimi. Belges* **1986**, *95*, 197.

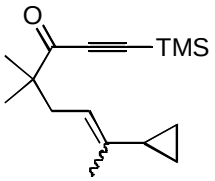
Additional signals for (*Z*)-olefin: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.52 (s, 1H), 5.15 (t, *J* = 7.5 Hz, 1H), 2.26 (d, *J* = 7.5 Hz, 1H), 1.65 (m, 1H), 1.42 (s, 3H), 1.09 (s, 6H), 0.62 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 138.7, 120.4, 35.6, 21.9, 19.7, 13.1, 4.9.



7-Cyclopropyl-4,4-dimethyl-1-trimethylsilyl-oct-6(*E*)-en-1-yn-3-ol: To a solution of trimethysilylacetylene (0.15 mL, 1.06 mmol) in THF (5 mL), at -78 ºC, was slowly added *n*-BuLi (0.7 mL, 1.6 M in hexanes, 1.12 mmol). After 1 h, the reaction mixture was added to a solution of 5-cyclopropyl-2,2-dimethyl-hex-4(*E*)-en-1-al (140 mg, 0.842 mmol) in THF (2 mL) at -78 ºC. After 4 h at -78 ºC, the reaction mixture was warmed to rt, quenched with 1N sodium bisulfate (50 mL) and extracted with diethyl ether (3 x 50 mL). The combined extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 8:1 petroleum ether: diethyl ether afforded the propargyl alcohol 7-cyclopropyl-4,4-dimethyl-1-trimethylsilyl-oct-6(*E*)-en-1-yn-3-ol: (193 mg, 87%) as a 2.5:1 mixture of *E*:*Z*-olefin isomers. The ratio of olefin isomers was determined by ^{1}H-NMR integration of the propargylic methine proton: for the *E*-isomer a doublet at 4.00 ppm (1H) and for the *Z*-isomer a doublet at 4.05 ppm (1H).

IR (film): 3443, 3083, 2962, 2873, 2171, 1470, 1384, 1251, 1053, 1002, 844, 760 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.23 (m, 1H), 4.00 (d, *J* = 6.2 Hz, 1H), 2.10 (dd, *J* = 14.1 and 8.2 Hz, 1H), 1.97 (dd, *J* = 14.1 and 7.5 Hz, 1H), 1.73 (d, *J* = 6.2 Hz, 1H), 1.47 (s, 3H), 1.23 (m, 1H), 0.90 (s, 6H), 0.49 (m, 2H), 0.38 (m, 2H), 0.11 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 138.7, 118.7, 105.6, 90.6, 70.8, 39.5, 36.2, 22.8(2), 19.1,14.1, 4.3, -0.1.

Additional signals for (*Z*)-olefin: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.26 (m, 1H), 4.05 (d, J = 6.1 Hz, 1H), 2.26 (dd, *J* = 14.1 and 8.2 Hz, 1H), 1.79 (d, *J* = 6.1 Hz, 1H), 1.72 (m, 1H), 1.36 (s, 3H), 1.90 (s, 6H), 0.53 (m, 2H), 0.10 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 121.4, 39.4, 35.6, 22.6, 19.0, 12.4, 4.0; HRMS (EI+) Calc'd for $C_{16}H_{28}OSi$: 264.1909. Found: 264.1910.



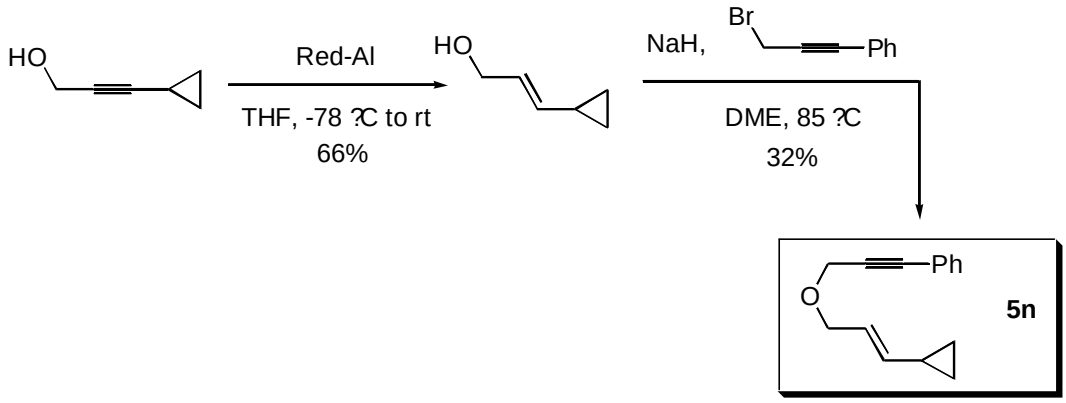
5m

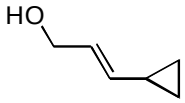
7-Cyclopropyl-4,4-dimethyl-1-trimethylsilyl-oct-6(*E*)-en-1-yn-3-one (**5m**): To a solution of 7-cyclopropyl-4,4-dimethyl-1-trimethylsilyl-oct-6(*E*)-en-1-yn-3-ol (40 mg, 0.151 mmol) and sodium bicarbonate (20 mg, 0.238 mmol) in methylene chloride (2 mL) was added Dess-Martin periodinane (80 mg, 0.189 mmol). After 1 h at rt, the white suspension was directly chromatographed eluting with 10:1 petroleum ether: diethyl ether to afford ketone **11.99** (34 mg, 85%) as a 2.4:1 mixture of *E*:*Z* olefin isomers. The ratio of olefin isomers was determined by ^{1}H-NMR integration of the allylic methine protons: for the *E*-isomer a doublet at 2.25 ppm (2H) and for the *Z*-isomer a doublet at 2.39 ppm (2H).

IR (film): 3084, 2968, 2151, 1671, 1469, 1385, 1252, 1073, 847, 762 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.05 (tm, *J* = 7.6 Hz, 1H), 2.25 (d *J* = 7.6 Hz, 2H), 1.44 (s, 3H), 1.29 (m, 1H), 1.08 (s,

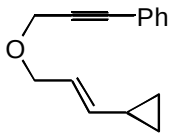
6H), 0.47 (m, 2H), 0.34 (m, 2H), 0.18 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 193.8, 138.7, 117.5, 100.4, 99.2, 48.7, 37.5, 23.4, 18.9,14.2, 4.4, -0.7.
Additional signals for (*Z*)-olefin: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.39 (d, *J* = 7.7 Hz, 2H), 1.60 (m, 1H), 1.34 (s, 3H), 1.12 (s, 6H), 0.53 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 137.8, 120.2, 99.1, 36.9, 23.5, 19.0, 12.4, 4.2; HRMS (EI+) Calc'd for $C_{16}H_{25}OSi$ (M - H^+): 261.1675. Found: 261.1678.

5n:





3-Cyclopropyl-prop-2(*E*)-en-1-ol:[22] To a solution of 3-cyclopropyl-prop-2-yn-1-ol[23] (1.0 g, 10.4 mmol) in THF (50 mL), at -78 ºC, was slowly added Red-Al (3.4 mL, 65 wt%, 10.6 mmol) and the solution allowed to warm to room temperature. After an additional 10 h, the clear yellow solution was quenched with 1N hydrochloric acid (100 mL) and extracted with diethyl ether (3 x 50 mL). The combined diethyl ether extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Kugelrohr distillation gave 3-cyclopropyl-prop-2(*E*)-en-1-ol (673 mg, 66 %) as a colorless liquid.
IR (film): 3620, 3080, 3020, 2930, 2870, 1670, 1470, 1430, 1390, 1370, 1195, 1080 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.75 (dt, *J* = 15.2 and 6.2 Hz, 1H), 5.23 (dd, *J* = 15.2 and 8.8 Hz, 1H), 4.09 (d, *J* = 6.2 Hz, 2H), 1.42 (m, 1H), 1.31 (br s, 1H), 0.74 (m, 2H), 0.40 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 137.4, 126.6, 63.6, 13.1, 6.5.



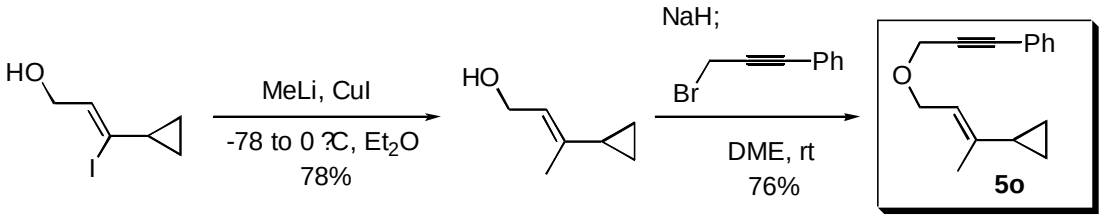
5n

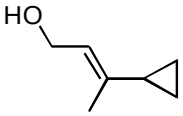
1-(3-Cyclopropylprop-2(*E*)-enyl-1-oxy)-3-phenylprop-2-yne (**5n**):[12] To a solution of 3-cyclopropyl-prop-2(*E*)-en-1-ol (50 mg, 0.51 mmol) in dimethoxyethane (5 mL) was added

[22] Ward, S.C.; Fleming, S.A. *J. Org. Chem.* **1994**, *59*, 6476.
[23] For preparation of this compound, see the preparation of **5g**, above.

sodium hydride (16 mg, 60% in mineral oil, 0.67 mmol) and the resulting white suspension stirred at room temperature for 1 h. To the suspension was added phenylpropargyl bromide (130 mg, 0.66 mmol) in dimethoxyethane (2 mL) and the solution heated at 85 ºC for 12 h. The resulting yellow solution was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 5% diethyl ether:petroleum ether gave 1-(3-cyclopropylprop-2(*E*)-enyl-1-oxy)-3-phenylprop-2-yne (35 mg, 32%) as a slightly yellow liquid.
IR (film): 3082, 2935, 2237, 1439, 1442, 1354, 1256, 1072, 1028, 757, 692 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.47 (m, 2H), 7.30 (m, 3H), 5.55 (dt, *J* = 15.1 and 6.8 Hz, 1H), 5.25 (dd, *J* = 15.1 and 8.9 Hz, 1H), 4.37 (s, 2H), 3.95 (dd, *J* = 6.8 and 1.0 Hz, 2H), 1.33 (m, 1H), 0.70 (m, 2H), 0.38 (m, 2H).

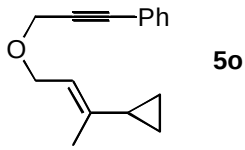
5o:





3-Cyclopropylbuten-2(*E*)-en-1-ol:[24] To a slurry of purified copper(+1) iodide (4.5 g, 23.6 mmol) in diethyl ether (40 mL), at -78 ºC was added MeLi (30 mL, 1.57 M in Et_2O, 47.2 mmol). The resulting suspension was warmed to 0 ºC resulting in the formation of a clear solution. After 15 min. at 0 ºC, the reaction mixture was recooled to -78 ºC and 3-cyclopropyl-3-iodo-prop-2(*Z*)-en-1-ol[25] (1.75 g, 7.82 mmol) in diethyl ether (5 mL) was added and the reaction mixture warmed to 0 ºC. After 12 h, the solution was quenched with 1M hydrochloric acid (100 mL) and the biphasic solution filtered through a pad of Celite, which was washed with diethyl ether (2 x 100 mL). The biphasic filtrate was separated, and the organic layer washed with brine (200 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 2:3 diethyl ether:petroleum ether afforded 3-cyclopropylbuten-2(*E*)-en-1-ol (680 mg, 78%) as a colorless liquid.
IR (film): 3333, 3083, 3007, 2919, 2872, 1660, 1428, 1386, 1240, 1000, 895, 816 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.35 (t, *J* = 6.8 Hz, 1H), 4.04 (d, *J* = 6.8 Hz, 2H), 2.38 (br s, 1H), 1.47 (s, 3H), 1.31 (m, 1H), 0.50 (m, 2H), 0.39 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 139.7, 121.7, 58.8, 18.5, 13.7, 4.4.

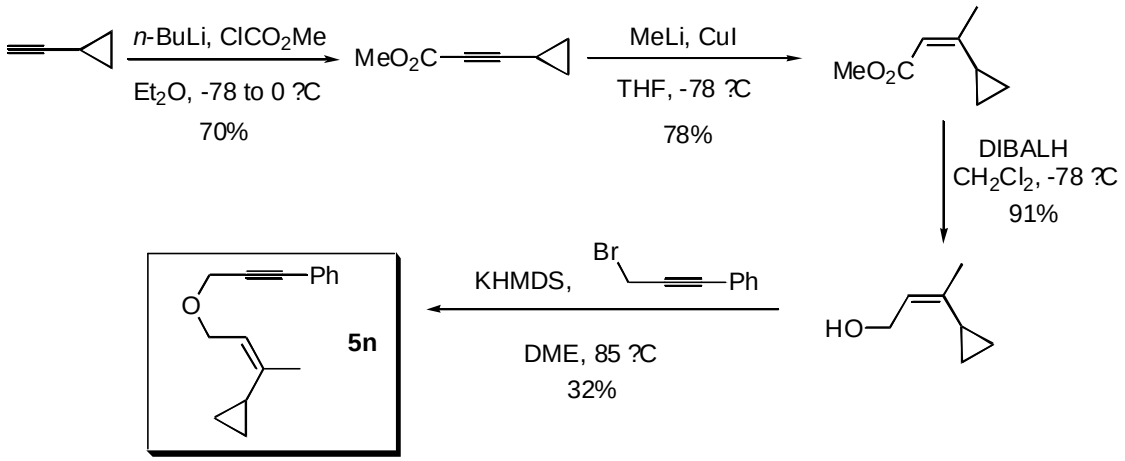
[24] Shvrin, K.N.; Krylova, I.V.; Shredova, I.B.; Okonnoshnikova, G.P.; Dolgii, I.E.; Nefedov, D.M. *J. Chem. Soc., Perkin Trans. 2* **1991**, *12*, 1875.
[25] For preparation of this compound, see the preparation of **5g**, above.

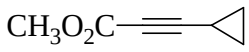


5o

1-(3-Cyclopropylbut-2(*E*)-enyl-1-oxy)-3-phenylprop-2-yne (**5o**):[22]**Fehler! Textmarke nicht definiert.** To a solution of 3-cyclopropylbuten-2(*E*)-en-1-ol (500 mg, 4.46 mmol) in dimethoxyethane (20 mL) was added sodium hydride (215 mg, 60% in mineral oil, 5.38 mmol) and the resulting white suspension stirred at room temperature 1 h. To the suspension was added phenylpropargyl bromide (810 mg, 4.46 mmol) in dimethoxyethane (5 mL) followed by sodium iodide (50 mg, 0.25 mmol). After stirring at 50 ºC for 12 h, the resulting yellow solution was diluted with 1N sodium bisulfate (100 mL), extracted with diethyl ether (3 x 50 mL), dried over ($MgSO_4$), and concentrated *in vacuo*. Flash chromatography eluting with 5% diethyl ether: petroleum ether gave **5o** (767 mg, 76%) as a slightly yellow liquid.
IR (film): 3082, 3005, 2935, 2849, 2236, 1662, 1490, 1442, 1354, 1256, 1072, 1028, 962, 924, 894, 757, 692 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.47 (m, 2H), 7.33 (m, 3H), 5.46 (t, *J* = 7.0 Hz, 1H), 4.38 (s, 2H), 3.97 (d, *J* = 7.0 Hz, 2H), 1.64 (s, 3H), 1.45 (m, 1H), 0.63 (m, 2H), 0.53 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 142.3, 131.6, 128.3, 128.2, 128.1, 122.7, 118.3, 85.9, 65.9, 57.5, 18.7, 14.1, 4.7.

5p:



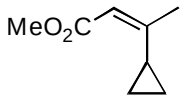


11.68

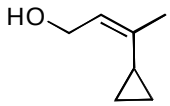
Methyl 3-cyclopropylpropynoate:[26] To a solution of cyclopropylacetylene (5.0 g, 75.8 mmol) in diethyl ether (100 mL), at -78 ºC, was added 1.5 M *n*-butyllithium (50 mL, 75.5 mmol) resulting in the formation of a thick white suspension which was warmed to 0 ºC over 1 h. To

[26] Piers, E.; Chong, J.M.; Morton, H.E. *Tetrahedron* **1989**, *45*, 363.

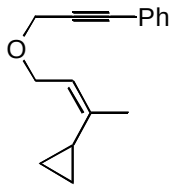
the suspension was added methyl chloroformate (8.7 mL, 113 mmol) and stirring continued at 0 ºC for 4 h. The white suspension was quenched with 1N sodium bisulfate (200 mL) and the biphasic solution separated and the aqueous layer extracted with diethyl ether (2 x 100 mL). The combined diethyl ether extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Kugelrohr distillation afforded methyl 3-cyclopropylpropynoate (6.6 g, 70%) as a colorless liquid.
IR (film): 2957, 2232, 1713, 1435, 1259, 1182, 1130, 1023, 860, 750 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.75 (s, 3H), 1.39 (m, 1H), 1.97-1.90 (m, 4H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 154.2, 93.5, 68.1, 52.4, 9.2, -0.7.



Methyl 3-cyclopropylbuten-2(*Z*)-en-1-oate: To a slurry of purified copper(+1) iodide (4.0 g, 21.0 mmol) in THF (100 mL), at -78 ºC, was added MeLi (25 mL, 1.6M in Et_2O, 40.0 mmol). The resulting suspension was warmed to 0 ºC resulting in the formation of a clear solution. After 15 min. at 0 ºC, the reaction mixture was recooled to -78 ºC and methyl 3-cyclopropylpropynoate (2.5 g, 20.2 mmol) in THF (10 mL) was added. After 1 h at -78 ºC, the solution was quenched with 1M sodium bisulfate (100 mL), warmed to room temperature and extracted with Et_2O (2 x 100 mL). The combined organic extracts were washed with brine (100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 10:1 petroleum ether:diethyl ether afforded methyl 3-cyclopropylbuten-2(*Z*)-en-1-oate (2.2 g, 78%) as a colorless liquid.
IR (film): 3091, 3012, 2950, 1715, 1630, 1447, 1253, 1194, 1159, 1112, 1076, 1032, 911, 843 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.73 (s, 1H), 3.67 (s, 3H), 3.21 (m, 1H), 1.51 (s, 3H), 0.84 (m, 2H), 0.75 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 167.4, 161.0, 115.7, 50.6, 18.5, 13.7, 6.7; HRMS (EI+) Calc'd for $C_8H_{12}O_2$: 140.0837. Found: 140.0835.



3-Cyclopropylbuten-2(*Z*)-en-1-ol:[19] To a solution of methyl 3-cyclopropylbuten-2(*Z*)-en-1-oate (1,4 g, 10.0 mmol) in CH_2Cl_2 (30 mL), at -78 ºC, was added 1.0 M di-*iso*-butylaluminum hydride (30 mL, 30.0 mmol). After stirring at -78 ºC for 12 h, the solution was quenched with ethyl acetate (2 mL), followed by saturated aqueous potassium sodium tartrate (50 mL). After stirring at room temperature for 2 h, the biphasic solution was separated and the aqueous layer extracted with diethyl ether (3 x 50 mL). The combined diethyl ether extracts were dried ($MgSO_4$), concentrated *in vacuo*, and chromatographed eluting with 2:3 diethyl ether:petroleum ether to afford 3-cyclopropylbuten-2(*Z*)-en-1-ol (1.02 g, 91%) as a colorless liquid.
IR (film): 3346, 3086, 3007, 2923, 2874, 1655, 1445, 1378, 1306, 1044, 995 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.48 (t, *J* = 7.0 Hz, 1H), 4.27 (d, *J* = 7.0 Hz, 2H), 1.90 (br s, 1H), 1.69 (m, 1H), 1.44 (s, 3H), 0.64 (m, 2H), 0.56 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 139.4, 124.5, 58.6, 18.6, 12.3, 4.3.

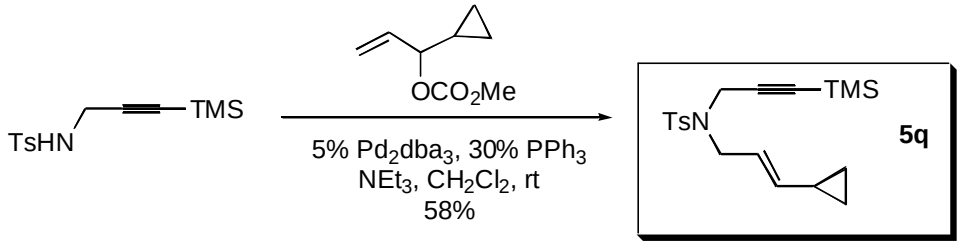


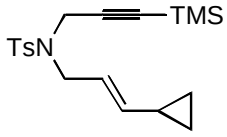
5p

1-(3-Cyclopropylbut-2(*Z*)-enyl-1-oxy) 3-phenylpro-2-yne (**5p**):[22] To a solution of 3-cyclopropylbuten-2(*Z*)-en-1-ol (500 mg, 4.46 mmol) in dimethoxyethane (20 mL) was added 0.5M potassium hexamethyldisilamide (9.4 mL, 4.7 mmol). The resulting yellow solution was stirred at room temperature for 5 min. then phenylpropargyl bromide (1.1 g, 5.64 mmol) in dimethoxyethane (5 mL) was added. The reaction was warmed to 85 ºC and stirred for 8 h. The resulting yellow solution was diluted with 1N sodium bisulfate (100 mL), extracted with diethyl ether (3 x 50 mL), dried over ($MgSO_4$), and concentrated *in vacuo*. Flash chromatography eluting with 20:1 petroleum ether:diethyl ether gave **5p** (322 mg, 32%) as a slightly yellow liquid.

IR (film): 3084, 3006, 2936, 2874, 2237, 1727, 1660, 1599, 1490, 1443, 1354, 1256, 1070, 757, 692 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.43 (m, 2H), 7.29 (m, 3H), 5.45 (t, *J* = 7.1 Hz, 1H), 4.37 (s, 2H), 4.27 (dd, *J* = 7.1 and 0.7 Hz, 2H), 1.76 (m, 1H), 1.46 (s, 3H), 0.64 (m, 2H), 0.58 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 142.6, 131.8, 128.4, 128.3, 128.2, 122.8, 121.2, 85.6, 65.5, 57.7, 18.9, 12.5, 4.5.

5q:





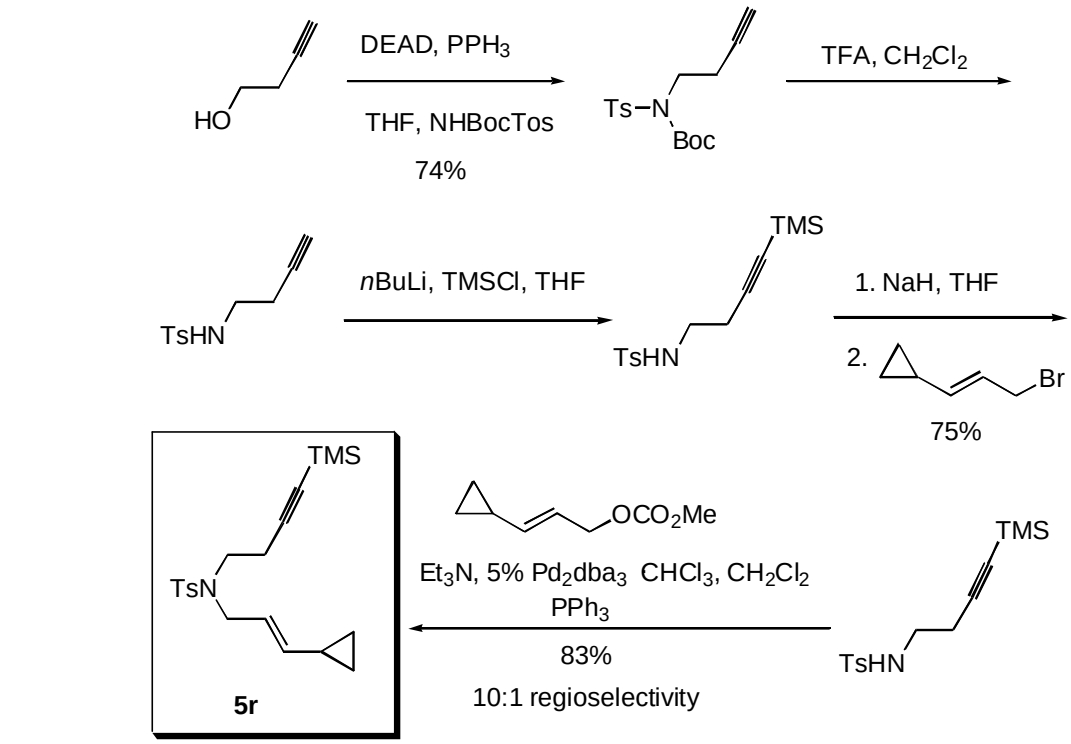
5q

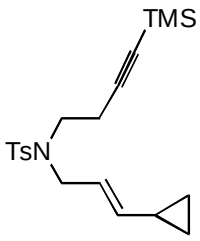
***N*-(3-Cyclopropyl-but-2-enyl)-*N*-(3-trimethylsilyl-prop-2-ynyl)-4-methyl-benzenesulfonamide** (**5q**): To a solution of 4-methyl-N-(3-trimethylsilanyl-prop-2-ynyl)-benzenesulfonamide[27] (350 mg, 1.25 mmol), Pd_2dba_3•$CHCl_3$ (65 mg, 0.063 mmol), and PPh_3 (98 mg, 0.37 mmol) in CH_2Cl_2 (3 mL) was added NEt_3 (0.35 mL, 2.62 mmol). After stirring at room temperature for 10 min, a solution of methyl (1-cyclopropylpro-2-en-1-yl)carbonate[14] (225 mg, 1.44 mmol) in CH_2Cl_2 was added (2 mL). After an additional 6 h, the solution was concentrated *in vacuo* and chromatographed eluting with 6:1 petroleum ether:diethyl ether to afford a 10:1 regioisomeric mixture of primary:secondary addition products. Recrystallization from hot petroleum ether gave **5q** (262 mg, 68%) as a white foam.

[27] Trost, B.M.; Toste, F.D. *J. Am. Chem. Soc.* **2002**, *124*, 5025.

IR (film): 3084, 3006, 2960, 2177, 1667, 1598, 1495, 1428, 1349, 1250, 1162, 1094, 1002, 964, 903, 845, 814, 740, 666 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 5.44 (dt, *J* = 15.2 and 6.9 Hz, 1H), 5.21 (dd, *J* = 15.2 and 8.7 Hz, 1H), 4.11 (s, 2H), 3.76 (d, *J* = 6.9 Hz, 2H), 2.44 (s, 3H), 1.41 (m, 1H), 0.74 (m, 2H), 0.37 (m, 2H), 0.00 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 143.2, 140.7, 136.0, 129.4, 127.8, 120.4, 98.0, 90.7, 48.2, 36.5, 21.5, 13.4, 6.9, -0.4; HRMS (EI+) Calc'd for $C_{19}H_{27}NO_2SSi$: 361.1532. Found: 361.1525.

5r:



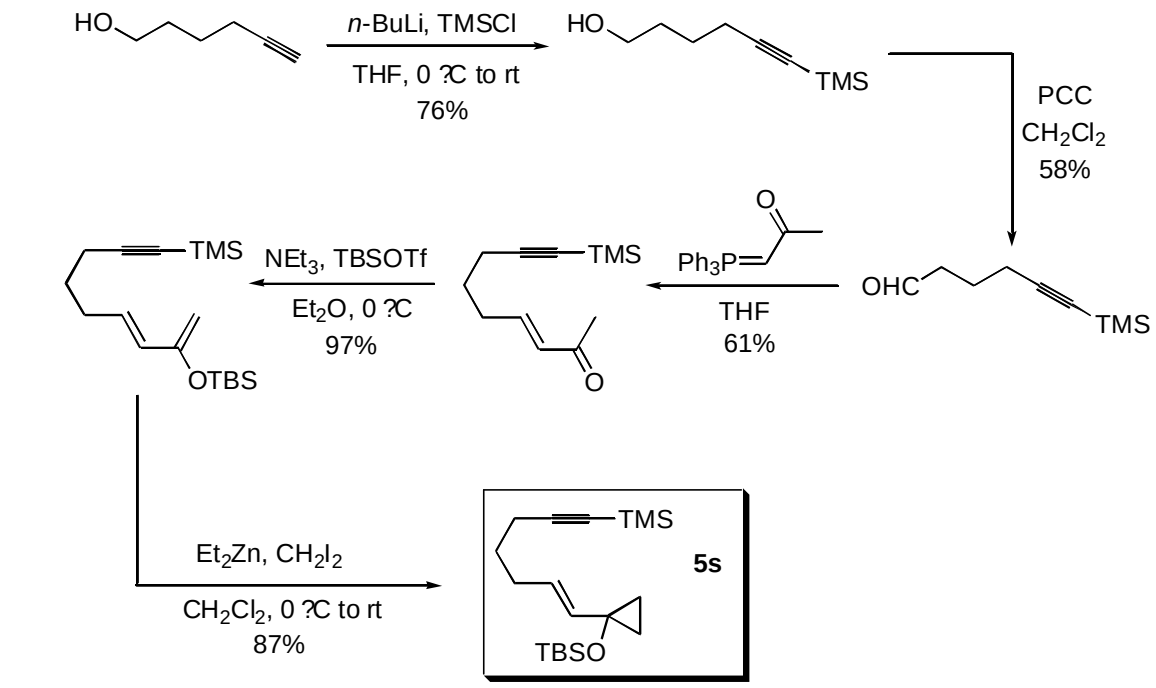


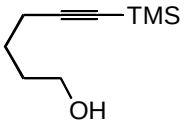
5r

***N*-(3-Cyclopropyl-allyl)-(4-trimethylsilyl-but-3-ynyl)-*p*-toluenesulfonamide** (**5r**): To a solution of *trans*-3-cyclopropylallyl alcohol (33mg, 0.34mmol) in 1 mL of distilled THF at −78 °C was added *n*-butyllithium (1.6 M in hexane, 0.23 mL, 0.37 mmol). The resulting solution was stirred for 10 min. to afford a bright yellow solution. To this solution was added distilled methanesulfonyl chloride (0.03 mL, 42 mg, 0.37 mmol) slowly followed by the addition of anhydrous lithium bromide (59 mg, dried at 100 °C in vacuum oven for 3 h) quickly. The mixture was stirred at −78 °C for 3.5 h to generate a bromide *in situ*, which was directly submitted to the next reaction without workup. In another flask containing a slurry of sodium hydride (15 mg, 60%, 0.37 mmol, washed with distilled hexane twice) in 0.5 mL of distilled THF at 0 °C over 15 min. was added a solution of 4-methyl-*N*-(4-trimethylsilyl-3-butynyl-benzenesulfonamide (100 mg, 0.34 mmol) in 1 mL of distilled THF to give a slightly cloudy solution. The solution of bromide generated *in situ* was then added to sulfonamide salt solution prepared by the procedures described above. The resulting yellow solution was stirred at rt overnight. The solution was diluted with 15 mL of diethyl ether, washed with 10 mL of water, and the organic

fraction was dried with anhydrous magnesium sulfate. After removing the solvent *in vacuo*, the residue was purified by flash chromatography eluting with 10%-50% diethyl ether in petroleum ether to afford **5r** (76 mg, 0.26 mmol, 75%) as a colorless oil.
IR (film) cm^{-1}: 3084w, 3006w, 2970w, 2177s, 1665w, 1599w, 1495w, 1451m, 1345s, 1250s, 1158s, 1095s, 1045m, 1020m, 950s, 920m, 843s, 815s, 760s, 719s, 700m; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.67(d, *J*=8.1 Hz, 2H), 7.27(d, *J*=7.8 Hz, 2 H), 5.28(dt, *J*=6.6, 15.6 Hz, 1H), 5.09(dd, *J*=8.7, 15.0 Hz, 1H), 3.76(d, *J*=6.0 Hz, 2H), 3.26 (t, *J*=7.5Hz, 2H), 2.46(t, *J*=7.5 Hz, 2H), 2.40(s, 3H), 1.30(m, 1H), 0.67(m, *J*=1.5, 6.3 Hz, 2H), 0.30 (m, *J*=1.5, 4.5Hz, 2H), 0.12 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 143.1, 139.7, 137.2, 129.6, 127.1, 121.5, 103.7, 86.4, 50.3, 45.5, 21.4, 20.7, 13.2, 7.2, 6.7, -0.06; HRMS: Calc'd for $C_{20}H_{29}O_2NSSi$: 375.1688. Found 375.1683.

5s:

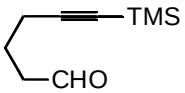




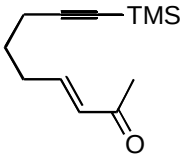
6-Trimethylsilanyl-hex-5-yn-1-ol:[28] To 5-hexyn-1-ol (4.0 g, 41 mmol) in 40 mL THF at -78 °C was added *n*-BuLi (58.2 mL, 1.4 M in hexanes, 81.5 mmol). The reaction was stirred 1 h at -78 °C then warmed to 0 °C and stirred 1 h. The reaction was recooled to -78 °C and TMSCl (9.31 g, 85.6 mmol) was added. The reaction was warmed to rt, stirred 1.5 h, then quenched with 10% HCl (100 mL) and allowed to stir vigourously 5 h. The reaction was extracted with 3 x 100 mL Et_2O, the organic layers combined, washed with 2 x 100 mL saturated aqueous $NaHCO_3$, 100 mL H_2O, and 100 mL saturated aqueous NaCl. The solution was concentrated *in*

[28] Harvey, D.F.; Lund, K.P.; Neil, D.A. *J. Am. Chem. Soc.* **1992**, *114*, 8424-8434.

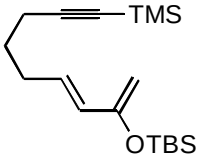
vacuo. The product was purified by flash chromatography (silica gel, 1:1 PE:Et_2O) to yield 6-trimethylsilanyl-hex-5-ynal (5.26 g, 30.88 mmol, 76% yield) as a clear, colorless oil.
R_f=0.25 (1:1 PE:Et_2O); IR (film) 3557, 2858, 2174, 1249, 1046k 844, 760, 698, 639 cm^{-1}; ^{1}H-NMR(300 MHz, $CDCl_3$) δ 3.66 (q, J= Hz, 2H), 2.25 (t, J= Hz, 2H), 1.68-1.55 (m, 4 H), 1.29 (t, J= Hz, 1H), 0.10 (s, 9H).



6-trimethylsilanyl-hex-5-ynal:[28] To a flask with PCC (9.91 g, 46 mmol) in 80 mL CH_2Cl_2 at 0 °C was added 6-trimethylsilanyl-hex-5-ynal (5.23 g, 30.7 mmol) in 20 mL CH_2Cl_2. Silica gel, 10 g, was added and the reaction warmed to rt and stirred 4.5 h. The suspension was gravity filtered, the solid washed with 2 x 100 mL Et_2O, and the combined filtrates extracted with 100 mL H_2O. The aqueous layer was extracted with 50 mL Et_2O, the organic layers combined and filtered through Fluorosil plug. The filtrates were concentrated *in vacuo* and the residue purified by flash chromatography (silica gel, 5:1 PE:Et_2O) to yield 6-trimethylsilanyl-hex-5-ynal (3.01 g, 17.9 mmol, 58% yield) as a clear, colorless oil.
R_f=0.87 (1:1 PE:Et_2O); IR (film) 2959, 2900, 2824, 2721, 2175, 1728, 1249, 843, 761, 699, 638 cm^{-1}; ^{1}H-NMR(300 MHz, $CDCl_3$) δ 9.79 (s, 1H), 2.56 (dt, J=7.3,1.2 Hz, 2H), 2.28 (t, J=6.8 Hz, 2H), 1.83 (m, 2H), 0.11 (s, 9H).

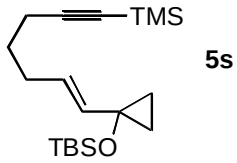


9-Trimethylsilanyl-non-3(*E*)-en-8-yn-2-one: To a 250 mL flask was added 6-trimethylsilanyl-hex-5-ynal (2.00 g, 11.88 mmol) followed by 100 mL THF and 1-triphenylphosphoranylidene-2-propanone (3.84 g, 12.06 mmol). The reaction was stirred for 21 h at rt. Water, 50 mL, was added and the aqueous solution extracted with Et_2O (3 x 100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated to yield a sticky brown solid. The oil was dissolved in 50 mL ether and the solid triphenylphosphine oxide was removed by filtration. This evaporation, dissolving, filtration sequence was repeated three times. The resulting residue was purified by flash chromatography (silica gel, 4:1 petroleum ether:ether) to yield 0.16 g recovered starting material (0.16g, 8% yield) and 9-trimethylsilanyl-non-3(*E*)-en-8-yn-2-one (1.51 g, 61% yield, 66% BRSM) exclusively as the *E*-olefin.
IR (film) 2959, 1687, 1650, 1587, 1250, 1050, 843, 760 cm^{-1}; ^{1}H-NMR(300 MHz, $CDCl_3$) δ 6.82-6.72 (m, 1H), 6.08 (d, J=15.8 Hz, 1H), 2.36-2.25 (m, 4H), 2.23 (s, 3H), 1.67 (m, 2H), 0.13 (s, 9H); ^{13}C-NMR(75 MHz, $CDCl_3$) δ 198.5, 147.1, 131.8, 106.1, 85.4, 31.3, 26.9, 19.3, 0.1; Anal Calc'd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67. Found: C, 69.51; H, 9.74.



2-(*tert*-Butyl-dimethyl-silanyloxy)-9-trimethylsilanyl-nona-1,3(*E*)-dien-8-yne: To a solution of 9-trimethylsilanyl-non-3(*E*)-en-8-yn-2-one (476 mg, 2.4 mmol) in 10 mL dry Et_2O at 0 °C

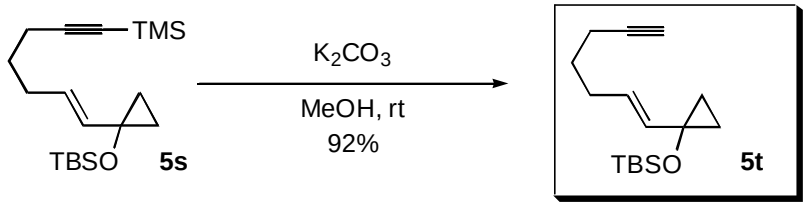
was added NEt_3 (725 mg, 7.1 mmol) and TBSOTf (1.24 g, 4.7 mmol). The reaction was stirred for 3 h at 0 °C. The reaction was poured into 50 mL brine, the organic layer was separated and then dried over Na_2SO_4. Concentration *in vacuo* yields a light yellow oil which was purified by flash chromatography (silica gel, 1% NEt_3 in petroleum ether) to give 2-(*tert*-Butyl-dimethyl-silanyloxy)-9-trimethylsilanyl-nona-1,3-dien-8-yne (741 mg , 97% yield) as a clear, light yellow oil.
IR (film) 2959, 2858, 2176, 1655, 1594, 1322, 1251, 964, 841, 810, 780, 760, 695, 640 cm^{-1}; ^{1}H-NMR (300 MHz, CDCl3) δ 6.0-5.82 (m, 2H), 4.20 (d, J=2.0 Hz, 2H), 2.20 (m, 4H), 1.60 (m, 2H), 0.95 (s, 9H), 0.15 (s, 6H), 0.13 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 162.1, 130.8, 127.6, 75.9, 80.1, 70.3, 32.1, 28.9, 21.0, 20.5, 14.8, 0.9, -3.1; Anal Calc'd for $C_{18}H_{34}OSi_2$: C, 67.01; H, 10.62. Found: C, 66.82; H, 10.39.

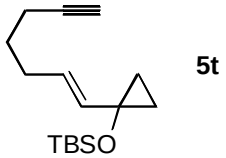


5s

1-(tert-butyl-dimethyl-silanyloxy)-1-(7-trimethylsilanyl-hept-1-en-6-ynyl)-cyclopropane (**5s**): To a solution of 2-(*tert*-Butyl-dimethyl-silanyloxy)-9-trimethylsilanyl-nona-1,3(*E*)-dien-8-yne (81.2 mg , 0.252 mmol) in 3 mL CH_2Cl_2 under argon was added diethylzinc (0.27 mL, 1.0 M in hexanes, 0.27 mmol) followed by dropwise addition of diiodomethane (64.8 mg, 0.242 mmol). The reaction was stirred at rt for 1 h. Ether, 5 mL, was added, the reaction mixture was poured into 5 mL saturated NH_4Cl, and the organic layer washed with 5 mL saturated $NaHCO_3$ then 5 mL H_2O. The organic layer was dried over $MgSO_4$ and concentrated to yield a light yellow oil. The product was purified by flash chromatography (silica gel, 50:1 petroleum ether:ether) to yield **5s** (71.2 mg, 87% yield) as a clear, light yellow oil.
IR (film) 3452, 2958, 2936, 2858, 2175, 1723, 1251, 1035, 842, 761 cm^{-1}; ^{1}H-NMR(300 MHz, $CDCl_3$) δ 5.58-5.48 (m, 1H), 5.31 (d, J=15.4 Hz, 1H), 2.20 (t, J=7.1 Hz, 2H), 2.09 (m, 2H), 1.54 (m, 2H), 0.85 (s, 9H), 0.64 (m, 1H), 0.13 (s, 9H) 0.08 (s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 134.9, 126.0, 107.2, 84.6, 56.5, 31.0, 28.3, 25.6, 19.2, 17.9, 15.3, 0.9, -3.7; Anal Calc'd for $C_{19}H_{36}OSi_2$: C, 67.78; H, 10.78. Found: C, 70.05; H, 10.55.

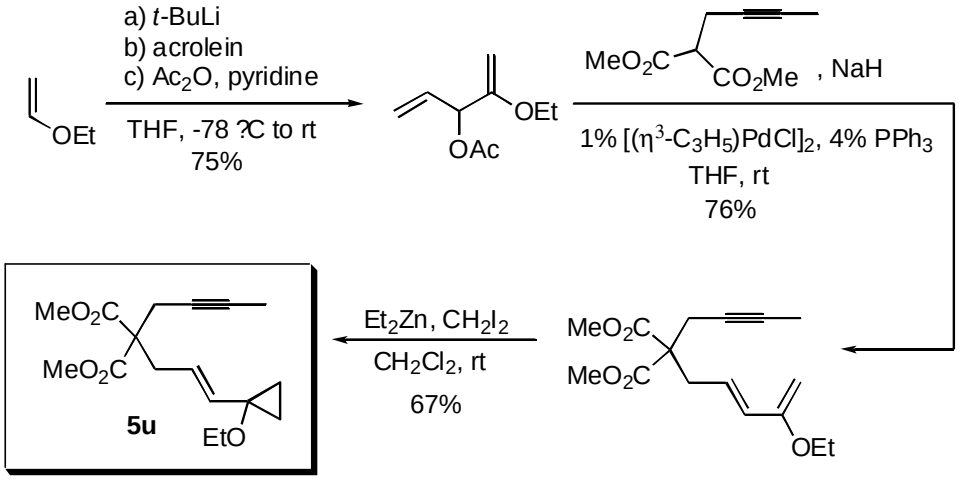
5t:

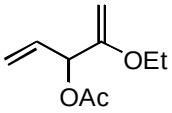




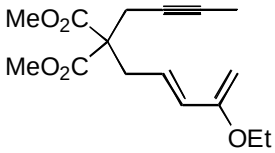
***tert*-Butyl-(1-hept-1-en-6-ynyl-cyclopropoxy)-dimethyl-silane** (**5t**): To a vial with **5u** (40 mg, 0.118 mmol) was added K_2CO_3 (200 mg, 1.45 mmol) and 0.5 mL MeOH. The reaction was stirred under air at rt 2 h. The reaction was diluted with 2 mL H_2O and extracted with 3 x 3 mL Et_2O, the organic layers were combined, dried over $MgSO_4$ and concentrated to yield **5t** (28.5 mg, 0.108 mmol, 92% yield) of sufficient purity to be used without purification.
IR (film) 2955, 1609, 1590, 1319, 1246, 1202, 973, 843 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.58-5.48 (m, 1H), 5.33 (d, J=15.4 Hz, 1H), 2.20 (t, J=7.3 Hz, 2H), 2.10 (m, 2H), 1.54 (m, 2H), 0.86 (s, 9H), 0.05 (s, 12H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 133.2, 124.1, 71.9, 60.1, 56.3, 32.1, 28.4, 20.9, 20.5, 15.1, 13.7, 1.0, -4.2; Anal Calc'd for $C_{19}H_{36}OSi_2$: C, 72.66; H, 10.67. Found: C, 73.07; H, 10.94.

5u:



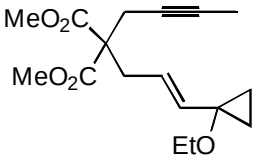


Acetic acid 2-ethoxy-1-vinyl-allyl ester:[29] To a solution of ethyl vinyl ether (8.10 g, 112.3 mmol) in 200 mL THF at -78 °C under argon balloon was added *tert*-butyllithium (60 mL, 1.7 M in *n*-pentane, 100 mmol) dropwise over 10 min. The reaction mixture was warmed to 0 °C at which time the reaction turned from yellow to colorless. The solution was cooled to -78 °C and a solution of acrolein (5.89 g, 105 mmol) in 10 mL THF was added dropwise over 5 min. The reaction was warmed to rt over 30 min. and stirred an additional 1.5 h. The mixture was cooled to 0 °C and a solution of acetic anhydride (20.5 g, 200 mmol) in pyridine (16.0 g, 202 mmol) was added. The cooling bath was removed and the reaction was stirred overnight at rt The resulting yellow slurry was worked up by addition of 5 mL MeOH to hydrolyze excess acetic anhydride. The resulting reaction mixture was poured into 100 mL sat. aq. NH_4Cl, and extracted with 3 x 100 mL ether. The combined organic layers were washed with 100 mL saturated aqueous $NaHCO_3$ and 100 mL H_2O. The organic layer was dried over $MgSO_4$ and concentrated to yield a clear, colorless oil. The product was purified by vacuum distillation (bp 75-85°C/5 mm Hg) to yield acetic acid 2-ethoxy-1-vinyl-allyl ester (12.89 g, 75.7 mmol, 76% yield) as a clear, colorless oil;
IR (film) 2983, 1747, 1634, 1445, 1372, 1299, 1232, 1118, 1071, 1023, 988, 817, 704, 609 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.91 (ddd, J=17.0, 10.5, 6.1 Hz, 1H), 5.59 (d, J=6.1 Hz, 1H), 5.32 (d, J=17.3 Hz, 1H), 5.22 (d, J=10.5 Hz, 1H), 4.18 (d, J=2.5 Hz, 1H), 4.02 (d, J=2.5 Hz, 1H), 3.74 (q, J=7.1 Hz, 2H), 2.09 (s, 3H).



2-But-2-ynyl-2-(4-ethoxy-penta-2,4-dienyl)-malonic acid dimethyl ester:[29] To a solution of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (11.8 mg, 0.32 mmol, 1 mol%) and PPh_3 (34.1 mg, 0.13 mmol, 4 mol%) in 40 mL THF was added acetic acid 2-ethoxy-1-vinyl-allyl ester (593 mg, 3.5 mmol). After 5 min., a solution of the sodium salt of maonate **A**[16] was added (650 mg, 3.5 mmol) [prepared by addition of **A** to 1 equivalent of NaH in 10 mL THF]. The reaction was stirred 15 h at rt then washed with 50 mL saturated aqueous NH_4Cl, saturated aqueous NaCl, and dried over $MgSO_4$. The solvent was removed *in vacuo*. Purification of the product by flash chromatography (silica gel, 5:1 PE:Et_2O) gives 2-but-2-ynyl-2-(4-ethoxy-penta-2,4-dienyl)-malonic acid dimethyl ester (912 mg, 3.1 mmol, 76% yield) as a clear, colorless oil.
R_f=0.58 (2:1 PE:Et_2O); IR (film) 3480, 2955, 1732, 1587, 1435, 1072, 976, 865, 816, 683 cm^{-1}; ^{1}H-NMR(300 MHz, $CDCl_3$) δ 5.99-5.87 (m, 2H), 4.06-4.00 (m, 2H), 3.77 (q, J=7.0 Hz, 2H), 3.74 (s, 6H), 2.87 (d, J=7.1 Hz, 2H), 2.90 (d, J=7.4 Hz, 2H), 2.83 (d, J=2.9 Hz, 2H), 2.01 (s, 1H), 1.28 (t, J=7.1 Hz, 3H).

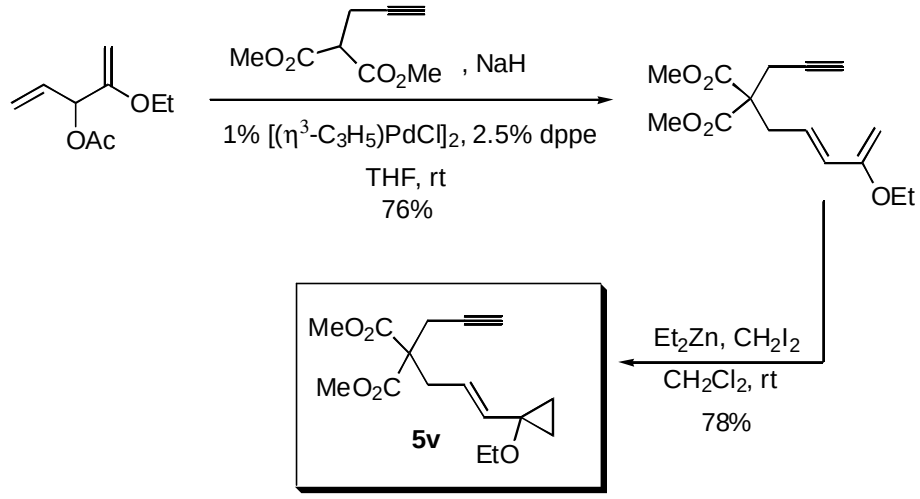
[29] Wender, P.A.; Dyckman, A.J.; Husfeld, C.O.; Kadereit, D.; Love, J.A.; Rieck, H. *J. Am. Chem. Soc.* **1999**, *121*, 10442.

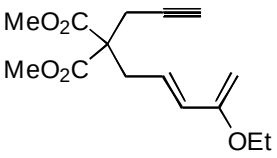


5v

2-But-2-ynyl-2-[3-(1-ethoxy-cyclopropyl)-allyl]-malonic acid dimethyl ester (**5v**):[29] To a solution of 2-but-2-ynyl-2-(4-ethoxy-penta-2,4-dienyl)-malonic acid dimethyl ester (426.2 mg, 1.45 mmol) in 15 mL CH_2Cl_2 under argon was added diethylzinc (1.4 mL, 1.0 M in hexanes, 1.4 mmol) followed by dropwise addition of diiodomethane (397 mg, 1.48 mmol). The reaction was stirred at rt for 12 h. The reaction mixture was poured into 20 mL saturated aqueous NH_4Cl and the organic layer was washed with 20 mL sat. aq. $NaHCO_3$ followed by 20 mL H_2O. The organic layer was dried over $MgSO_4$ and concentrated to yield a light yellow oil. The product was purified by flash chromatography (silica gel, 4:1 petroleum ether:ether) to give **5v** (288 mg, 0.93 mmol, 67% yield) as a clear, colorless oil.
IR (film) 2976, 2955, 1738, 1438, 1391, 1286, 1226, 1203, 1063, 977 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.48-5.36 (m, 2H), 3.73 (s, 6H), 3.44 (q, J=7.1 Hz, 2H), 2.77 (d, J=6.4 Hz, 2H), 2.73 (d, J=2.5 Hz, 2H), 1.76(t, J=2.5 Hz, 1H), 1.14 (t, J=7.1 Hz, 3H) 0.96 (m, 2H). 0.63 (m, 2H).

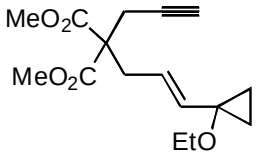
5v:





2-(4-Ethoxy-penta-2,4-dienyl)-2-prop-2-ynyl-malonic acid dimethyl ester:[29] To a solution of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (11.8 mg, 0.32 mmol, 1 mol%) and bis(diphenylphosphino)ethane (32 mg, 0.081 mmol, 2.5 mol%) in 40 mL THF was added acetic acid 2-ethoxy-1-vinyl-allyl ester (550 mg, 3.2 mmol). After 5 min., a solution of the sodium salt of maonate **B**[14] (599 mg, 3.5 mmol) was added [prepared by addition of malonate **B** to 1 equivalent of NaH in 10 mL THF]. The reaction was stirred 15 h at rt then washed with 50 mL saturated aqueous NH_4Cl, saturated aqueous NaCl, and dried over $MgSO_4$. The solvent was removed *in vacuo*. Purification of the

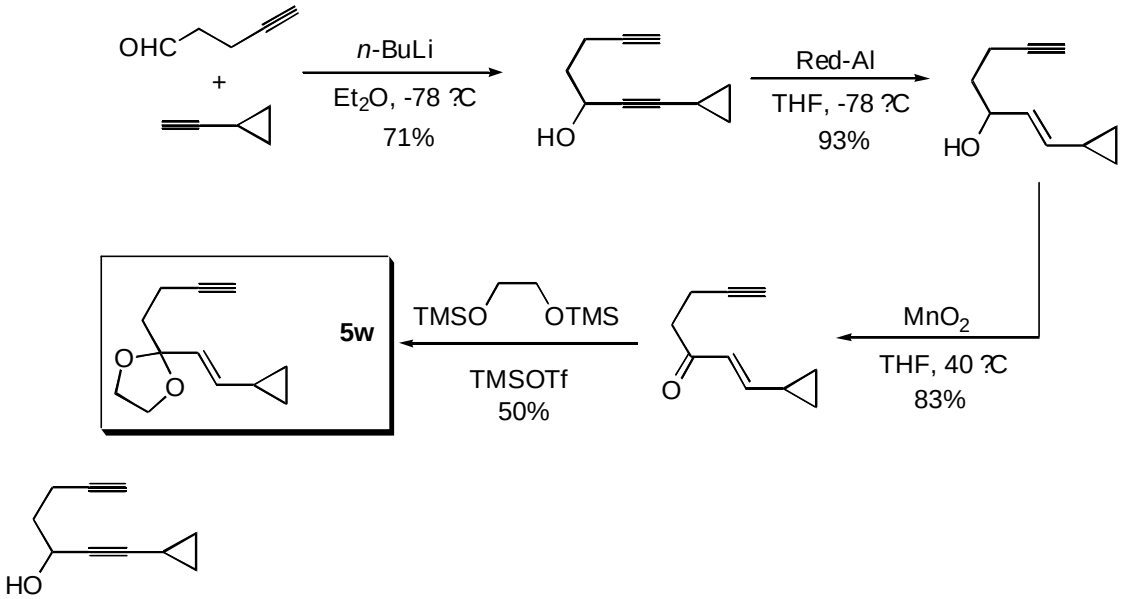
product by flash chromatography (silica gel, 5:1 PE:Et_2O) gives 2-(4-ethoxy-penta-2,4-dienyl)-2-prop-2-ynyl-malonic acid dimethyl ester (684 mg, 2.4 mmol, 76% yield) as a clear, colorless oil. R_f=0.58 (2:1 PE:Et_2O); IR (film) 3285, 2958, 1732, 1437, 1207 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.99-5.85 (m, 2H), 4.06-4.00 (m, 2H), 3.77 (q, J=7.1 Hz, 2H), 374 (s, 6H), 2.87 (d, J=7.1 Hz, 2H), 2.80 (d, J=3.0 Hz, 2H), 2.06 (s, 1H), 1.31 (t, J=7.1 Hz, 3H).



5v

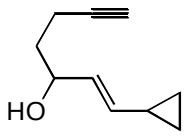
2-[3-(1-Ethoxy-cyclopropyl)-allyl]-2-prop-2-ynyl-malonic acid dimethyl ester (**5v**):[29] To a solution of 2-(4-ethoxy-penta-2,4-dienyl)-2-prop-2-ynyl-malonic acid dimethyl ester (437 mg, 1.56 mmol) in 15 mL CH_2Cl_2 under argon was added diethylzinc (1.4 mL, 1.0 M in hexanes, 1.4 mmol) followed by dropwise addition of diiodomethane (380 mg, 1.40 mmol). The reaction was stirred at rt for 12 h. The reaction mixture was poured into 20 mL saturated NH_4Cl, and the organic layer washed with 20 mL saturated $NaHCO_3$ and 20 mL H_2O. The organic layer was dried over $MgSO_4$ and concentrated to yield a light yellow oil. The product was purified by flash chromatography (silica gel, 4:1 petroleum ether:ether) to yield **5v** (321 mg, 1.09 mmol, 78% yield) as a clear, colorless oil; IR (film) 2977, 2955, 1737, 1438, 1286, 1062, 977 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.47-5.36 (m, 2H), 3.74 (s, 6H), 3.44 (q, J=7.0 Hz, 2H), 2.82-2.79 (m, 4H), 2.02 (t, J=2.7 Hz, 1H), 1.15 (t, J=7.2 Hz, 3H), 0.97 (m, 2H), 0.64 (m, 2H).

5w:

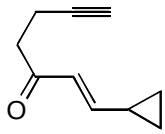


1-Cyclopropyl-hepta-1,6-diyn-3-ol: To a solution of cyclopropylacetylene (2.0 g, 30.3 mmol) in diethyl ether (100 mL), at -78 ºC, was added 1.5 M *n*-butyllithium (20 mL, 30.0 mmol) resulting in the formation of a thick white suspension which was warmed to room temperature over 1 h. The suspension was recooled to -78 ºC and a solution of pent-4-ynal (2.0 g, 24.4 mmol) in diethyl ether (10 mL) was added. The white suspension was washed with 1N sodium

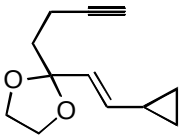
bisulfate (2 x100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Kugelrohr distillation afforded 1-cyclopropyl-hepta-1,6-diyn-3-ol (3.19 g, 71%) as a colorless liquid
IR (film): 3366 3298, 3012, 2934, 2241, 2118, 1430, 1060, 1019, 908 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.49 (q, *J* = 6.0 Hz, 1H), 2.44-2.30 (m, 2H), 1.87 (dd, *J* = 5.3 Hz, 1H), 1.23 (t, *J* = 2.5 Hz 1H), 1.88 (m, 2H), 1.26 (m, 1H), 0.79 (m, 2H), 0.69 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 89.2, 83.5, 75.4, 68.8, 61.4, 36.5, 14.5, 8.2, -0.7. Anal. Calc'd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.86; H, 7.96.



7-Cyclopropyl-hept-6(*E*)-en-1-yn-5-ol: To a solution of 1-cyclopropyl-hepta-1,6-diyn-3-ol (500 g, 3.37 mmol) in THF (20 mL), at -78 ºC, was slowly added 65 wt% Red-Al (2.0 mL, 6.74 mmol) and the solution allowed to warm to room temperature. After an additional 10 h, the clear yellow solution was quenched with 1N hydrochloric acid (100 mL) and extracted with diethyl ether (3 x 100 mL). The combined diethyl ether extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 1:1 petroleum ether:diethyl ether afforded 7-cyclopropyl-hept-6(*E*)-en-1-yn-5-ol (470 mg, 93%) as a colorless liquid.
IR (film): 3375, 3303, 3062, 3006, 2925, 2868, 2117, 1666, 1430, 1100, 1049, 1021, 964, 940, 813 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.54 (dd, *J* = 15.3 and 7.1 Hz, 1H), 5.22 (dd, *J* = 15.3 and 8.8 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 1H), 2.36-1.22 (m, 2H), 1.97 (t, *J* = 2.7 HZ, 1H), 1.82-1.67 (m, 3H), 1.39 (m, 1H), 0.73 (m, 2H), 0.38 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 136.5, 129.5, 84.0, 71.6, 35.6, 14.7, 13.4, 6.8, 6.7. Anal. Calc'd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.14; H, 9.16.



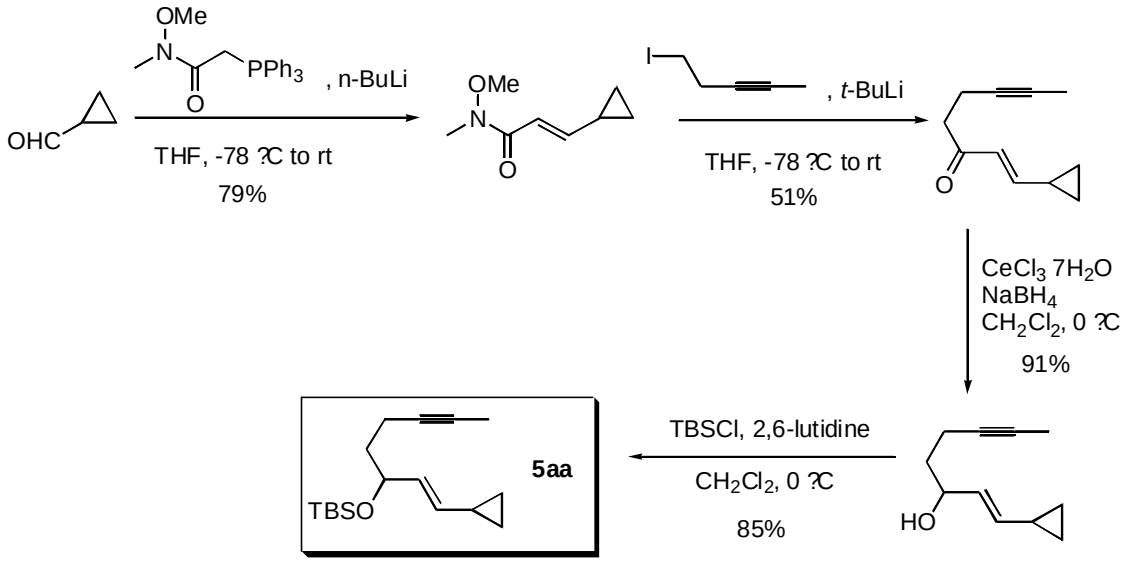
7-Cyclopropyl-hept-6(*E*)-en-1-yn-5-one: A solution of 7-cyclopropyl-hept-6(*E*)-en-1-yn-5-ol (385 mg, 2.56 mmol) and manganese dioxide (2.2g, 25.3 mmol) in THF (13 mL) was heated at 40 ºC. After 2 h, the black suspension was filtered through a pad of silica, which was flushed with diethyl ether (3 x 25 mL). The combined diethyl ether extracts were washed with brine (50 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 1:1 petroleum ether:diethyl ether afforded 7-cyclopropyl-hept-6(*E*)-en-1-yn-5-one (315 mg, 83%) as a colorless liquid.
IR (film): 3300, 3009, 2921, 2119, 1687, 1662, 1620, 1432, 1381, 1261, 1200, 1150, 1098, 1055, 976, 954, 936, 807 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.36 (dd, *J* = 15.7 and 6.9 Hz, 1H), 6.24 (d, *J* = 15.7 Hz, 1H), 2.78 (t, *J* = 7.1 Hz, 2H), 2.50 (td, *J* = 7.1 and 2.6 Hz, 2H), 1.96 (t, *J* = 2.7 Hz, 1H), 1.60 (m, 1H), 1.01 (m, 2H), 0.70 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 196.9, 153.3, 126.8, 83.4, 68.6, 38.8, 14.8, 13.1, 9.1.

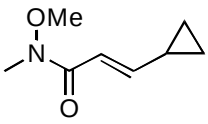


5w

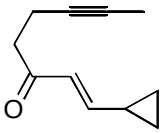
2-(But-3-ynyl)-2-(2-cyclopropylvinyl)-[1,3]dioxolane (**5w**): To a solution of trimethylsilyl triflate (15 mg, 0.068 mmol) in dichloromethane (7 mL), -78 ºC was added 1,2-bis(trimethylsiloxy)ethane (558 mg, 2.70 mmol) followed by a solution of 7-cyclopropyl-hept-6(*E*)-en-1-yn-5-one (200 mg, 1.35 mmol) in methylene chloride (1 mL). The reaction mixture was allowed to warm to room temperature, stirred for 10 h, and then quenched with pyridine (1 mL). The reaction mixture was diluted with 1N sodium bicarbonate (25 mL), and extracted with diethyl ether (3 x 25 mL). The combined diethyl ether extracts were washed with 10% copper sulfate (50 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 8:1 petroleum ether: diethyl ether afforded **5w** (130 mg, 50%) as a colorless liquid.
IR (film): 3302, 3082, 2960, 2887, 2118, 1655, 144, 1370, 1252, 1203, 1122, 1042, 971, 948, 902 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.38 (d, *J* = 15.4 Hz, 1H), 5.29 (dd, *J* = 15.4 and 9.0 Hz, 1H), 3.92-3.82 (m, 1H), 2.24 (m, 2H), 1.93 (m, 2H), 1.89 (t, *J* = 2.7 Hz, 1H), 1.35 (m, 1H), 0.70 (m, 2H), 0.36 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 136.3, 126.3, 108.0, 84.4, 67.7, 64.5, 37.3, 13.1, 12.9, 6.9. Anal Calc'd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.07; H, 8.55.

Substrates in Table 2:
5aa:

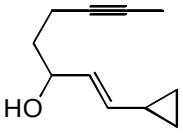




3-Cyclopropyl-*N*-methoxy-*N*-methyl-acrylamide:[30] To a solution of diethyl (*N*-methoxy-*N*-methylcarbamoxylmethyl)phosphonate (1.75 g, 7.32 mmol) in THF (5 mL), at -78 ºC, was added 1.5M *n*-butyllithium (4.9 mL, 7.35 mmol). After stirring at -78 ºC for 30 min., cyclopropanal (0.5 mL, 6.69 mmol) in THF (2 mL) was added and the reaction mixture slowly warmed to room temperature. After an additional 4 h, the reaction mixture was quenched with 1N sodium bisulfate (50 mL) and extracted with diethyl ether (3 x 25 mL). The combined extracts were dried ($MgSO_4$), concentrated *in vacuo* and chromatographed eluting with 1:1 diethyl ether: petroleum ether to afford 3-cyclopropyl-*N*-methoxy-*N*-methyl-acrylamide (820 mg, 79%) as a colorless liquid.
IR (film): 3085, 3006, 2936, 1660, 1626, 1422, 1386, 1351, 1179, 1097, 1007, 959, 939, 879 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.48 (d, *J* = 15.2 Hz, 1H), 6.39 (dd, *J* = 15.2 and 9.9 Hz, 1H), 3.69 (s, 3H), 3.21 (s, 3H), 1.59 (s, 1H), 0.70 (m, 2H), 0.62 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 166.9, 152.4, 115.5, 61.5, 32.2, 14.6, 8.3.



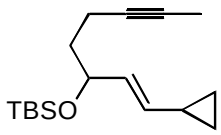
8-Cyclopropyl-oct-7(*E*)-en-2-yn-6-one: To a solution of 5-iodo-pent-2-yne (200 mg, 1.03 mmol) in THF (10 mL), at -78 ºC, was added 1.5M *tert*-butyllithium (1.4 mL, 2.10 mmol). After 15 min. at -78 ºC, the resulting dark orange solution was treated with a solution of 3-cyclopropyl-*N*-methoxy-*N*-methyl-acrylamide (106 mg, 0.683 mmol) in THF (1 mL) and slowly warmed to room temperature. After an additional 4 h, the solution was diluted with diethyl ether (25 mL), washed with 1N sodium bisulfate (2 x 25 mL), brine (25 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 5:1 petroleum ether: diethyl ether afforded ketone 8-cyclopropyl-oct-7(*E*)-en-2-yn-6-one (84 mg, 51%) as a colorless liquid.
IR (film): 3006, 2920, 1709, 1692, 1667, 1620, 1430, 1380, 1197, 1095, 976, 938 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.34 (dd, *J* = 15.6 and 9.9, 1H), 6.23 (d, *J* = 15.6 Hz, 1H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.44 (m, 2H), 1.78 (t, *J* = 2.5 Hz, 3H), 1.59 (m, 1H), 1.01 (m, 2H), 0.69 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 198.4, 153.7, 127.7, 78.7, 76.7, 40.1, 15.5, 14.3, 9.7, 4.2; HRMS (EI+) Calc'd for $C_{11}H_{14}O$: 162.1045. Found: 162.1035.



8-Cyclopropyl-oct-7(*E*)-en-2-yn-6-ol: To a solution of 8-cyclopropyl-oct-7(*E*)-en-2-yn-6-one (100 mg, 0.617 mmol) and cerium trichloride (230 mg, 0.649 mmol) in methanol (5 mL), at 0 ºC, was slowly added sodium borohydride (25 mg, 0.661 mmol). After 1 h at 0 ºC, methylene chloride (25 mL) was added and the white suspension filtered through a pad of silica. The filtrate was washed with 1N sodium bisulfate (2 x 25 mL), brine (25 mL), dried ($MgSO_4$), concentrated *in vacuo*. Flash chromatography eluting with 6:1 petroleum ether: diethyl ether afforded 8-cyclopropyl-oct-7(*E*)-en-2-yn-6-ol (92 mg, 91%) as a colorless liquid.

[30] Wender, P.A.; Fuji, M.; Husfeld, C.O.; Love, J.A. *Org. Lett.* **1999**, *1*, 137.

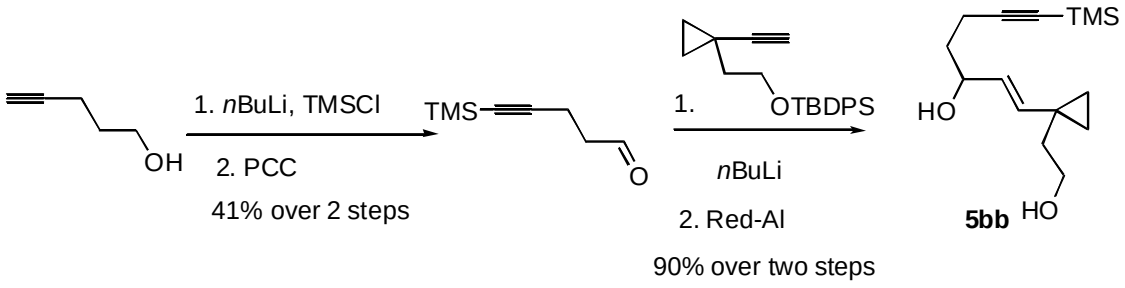
IR (film): 3364, 3005, 2919, 2859, 1666, 1433, 1098, 1047, 963, 812 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.56 (dd, *J* = 15.3 and 6.9, 1H), 5.24 (d, *J* = 15.3 and 8.7 Hz, 1H), 4.20 (q, *J* = 6.9 Hz, 1H), 2.24 (m, 2H), 1.80 (dd, *J* = 2.6 and 1.6 Hz, 3H), 1.70 (m, 3H), 1.40 (m, 1H), 0.74 (m, 2H), 0.41 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 136.1, 129.8, 78.6, 76.1, 71.9, 36.2, 15.1, 13.4, 6.8 3.5; HRMS (EI+) Calc'd for $C_{11}H_{15}O$ ($M - H^+$): 163.1123. Found: 163.1124.

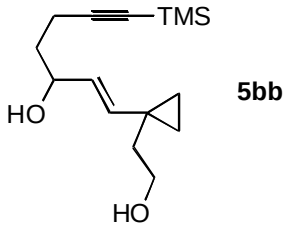


5aa

8-Cyclopropyl-6-(*tert*-butyldinethylsilyloxy)-oct-7(*E*)-en-2-yne (**5aa**): To a solution of 8-cyclopropyl-oct-7(*E*)-en-2-yn-6-ol (50 mg, 0.305 mmol) in methylene chloride (3 mL), at 0 ºC, was added 2,6-lutidine (0.12 mL, 1.03 mmol) followed by *tert*-butyldimethylsilyl triflate (0.12 mL, 0.523 mmol). After 4 h at 0 ºC, diethyl ether (25 mL) and the solution washed with 1N sodium bisulfate (2 x 25 mL), brine (25 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 6:1 petroleum ether: diethyl ether afforded alcohol **5aa** (72 mg, 85%) as a colorless liquid.
IR (film): 29555, 2928, 2857, 1667, 1472, 1361, 1254, 1085, 1054, 962, 836, 776 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.46 (dd, *J* = 15.4 and 6.8, 1H), 5.13 (d, *J* = 15.4 and 8.6 Hz, 1H), 4.16 (q, *J* = 6.8 Hz, 1H), 2.18 (m, 2H), 1.79 (t, *J* = 2.6 Hz, 3H), 1.70-1.57 (m, 2H), 1.37 (m, 1H), 0.90 (s, 9H), 0.70 (m, 2H), 0.36 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 134.4, 130.5, 79.1, 75.5, 72.1, 37.6, 18.2, 14.8, 13.2, 6.5, 6.4, 3.5, -4.2, -4.9. Anal Calc'd for $C_{17}H_{30}OSi$: C, 73.31; H, 10.86. Found: C, 72.98; H, 10.75.

5bb:





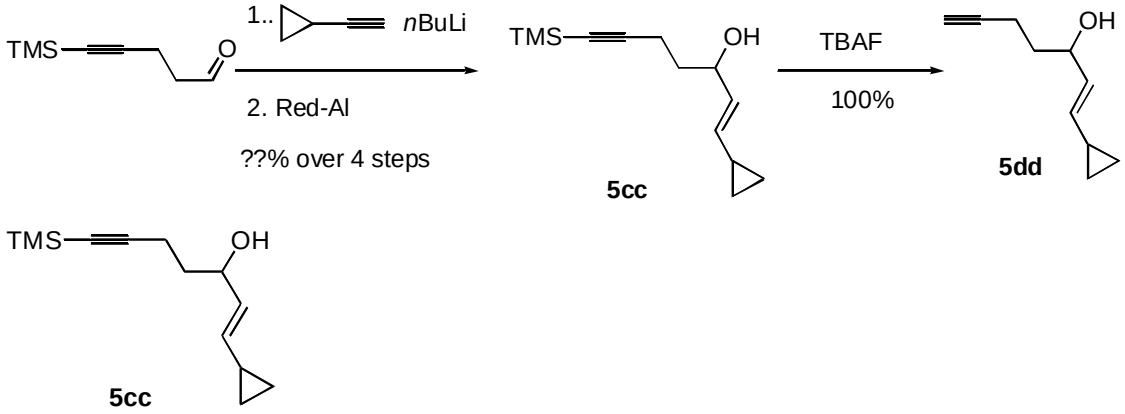
5bb

1-[(1*E*)-3-hydroxy-7-(trimethylsilyl)-1-hepten-6-ynyl]-cyclopropaneethanol (**5bb**): To a solution of 4-pentyn-1-ol (3.3 g, 39.2 mmol) in 50 mL of THF at -78ºC was added *n*BuLi (36 mL, 2.5 M in hexane). After 1 h, to this solution was added TMSCl (10.6 g, 12.4 mL, 98 mmol). The solution was warmed to rt over 2h and quenched with water (100 mL). The aqueous solution was extracted with diethyl ether (50 mLx3). The combined organic layer was dried with magnesium sulphate and concentrated in vacuo. Flash chromatography eluting with 5-20%

diethyl ether in petroleum ether afforded 5-trimethylsilyl-4-pentyn-1-ol (4.9 g, 31.4 mmol). The alcohol was then submitted to a slurry of PCC (13.6 g, 62.8 mmol) in 50 mL of dichloromethane at 0°C. The slurry was warmed to rt over 1h and stirred for additional 5h. Filtration followed by concentration in vacuo afforded brown oil, which was further purified by flash chromatography eluting with 5% diethyl ether in petroleum ether to afford 5-trimethylsilyl-4-pentynal (2.5 g, 16.2 mmol, 41% over 2 steps) as a light brown oil. To a solution of *tert*-butyl-[2-(1-ethynylcyclopropyl)-ethoxy]-diphenylsilane (35 mg, 0.10 mmol) in 0.5 mL of THF was added *n*BuLi (0.11 mmol, 70 uL, 1.6 M in hexane) at -78°C. After 30 min, to this solution was added a solution of 5-trimethylsilyl-4-pentynal (13 mg, 0.084 mmol) in 0.5 mL of THF. The mixture was slowly warmed to rt over 2h. The mixture was directly purified by flash chromatography eluting with 5% to 10% diethyl ether in petroleum ether to give 1-{1-[2-(*tert*-butyldiphenylsiloxyethyl)-cyclopropyl]-trimethylsilyl-hepta-1,6-diyn-3-ol (42 mg, 0.084 mmol) as a clear oil, which was then dissolved in THF (3 mL). To this solution was added Red-Al (65 mg, 0.21 mmol, 65% in toluene) at 0°C. The reaction mixture was warmed to rt and stirred for 2h. It was quenched by the addition of an aqueous solution of Rochelle's salt (1 mL) and chromatographed directly on silica gel eluting with 5% diethyl ether in petroleum ether to diethyl ether to afford **5bb** (20 mg, 0.075 mmol, 90%) as a colorless oil.

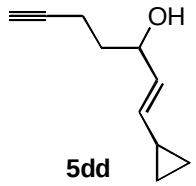
IR (neat): 3363bm, 3078w, 2927s, 2174m, 1664w, 1427w, 1250m, 1052m, 843s cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.60-5.35 (m, 2H), 4.25-4.15 (m, 1H), 3.80-3.68 (m, 2H), 2.36-2.21 (m, 2H), 1.80-1.60 (m, 5H), 1.33-1.15 (m, 3H), 0.68-0.54 (m, 4H), 0.14 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 137.0, 129.0, 106.7, 85.2, 72.0, 61.4, 39.1, 35.8, 29.7, 18.9, 16.2, 13.8, 0.1; HRMS: Calc'd for $C_{15}H_{26}O_2Si$ (M^+): 266.1702. Found: 266.1704.

5cc, 5dd:



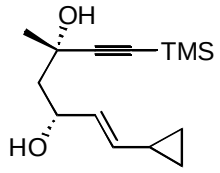
1-Cyclopropyl-7-trimethylsilyl-1-hepten-6-yn-3ol (5cc): To a solution of 5-trimethylsilyl-4-pentynal (2.2 g, 14.3 mmol) in 15 mL of THF was added a lithium cyclopropyl acetylene solution. (The lithium solution of cyclopropyl acetylene was prepared by the addition of *n*BuLi (8.6 mL, 2.5 M in hexane, 21.4 mmol) to a 10 mL THF solution of cyclopropyl acetylene at -78°C and stirred for 30 min at this temperature.) The resulting solution was slowly warmed to rt overnight. After removal of solvent, the residue was purified by flash chromatography (10% diethyl ether in petroleum ether) to afford diyne (2.2 g, 10.0 mmol, 70%) as a light brown oil. To a 15 mL of THF solution of this diyne (2.2 g, 10.0 mmol) was added Red-Al (20.0 mmol) at -78°C. The mixture was slowly warmed to 0°C and stirred for 6h at this temperature. The resulting mixture was quenched with an aqueous solution of Rochelle's salt at rt. The aqueous

layer was extracted with diethyl ether (50 mL x 3). The combined organic layers were dried with magnesium sulphate and concentrated in vacuo. The residue was purified by flash chromatography eluting with 15% diethyl ether in petroleum ether to afford **5cc** (1.4 g, 6.3 mmol, 63%) as a light brown oil.
IR (neat): 3356, 2958, 2174, 1250, 963, 843 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.53 (dd, *J*=15.4, 7.1 Hz, 1H), 5.19 (dd, *J*=15.4, 8.8 Hz, 1H), 4.16 (m, 1H), 2.31 (m, 2H), 1.78-1.65 (m, 3H), 1.37 (dtt, *J*=8.8, 8.1, 4.9 Hz, 1H), 0.71 (m, 2H), 0.36 (m, 2H), 0.14 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 136.3, 129.6, 106.9, 85.1, 71.9, 35.8, 16.3, 13.4, 6.8, 0.1. Anal. Calc'd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 70.37; H, 10.05.



5dd

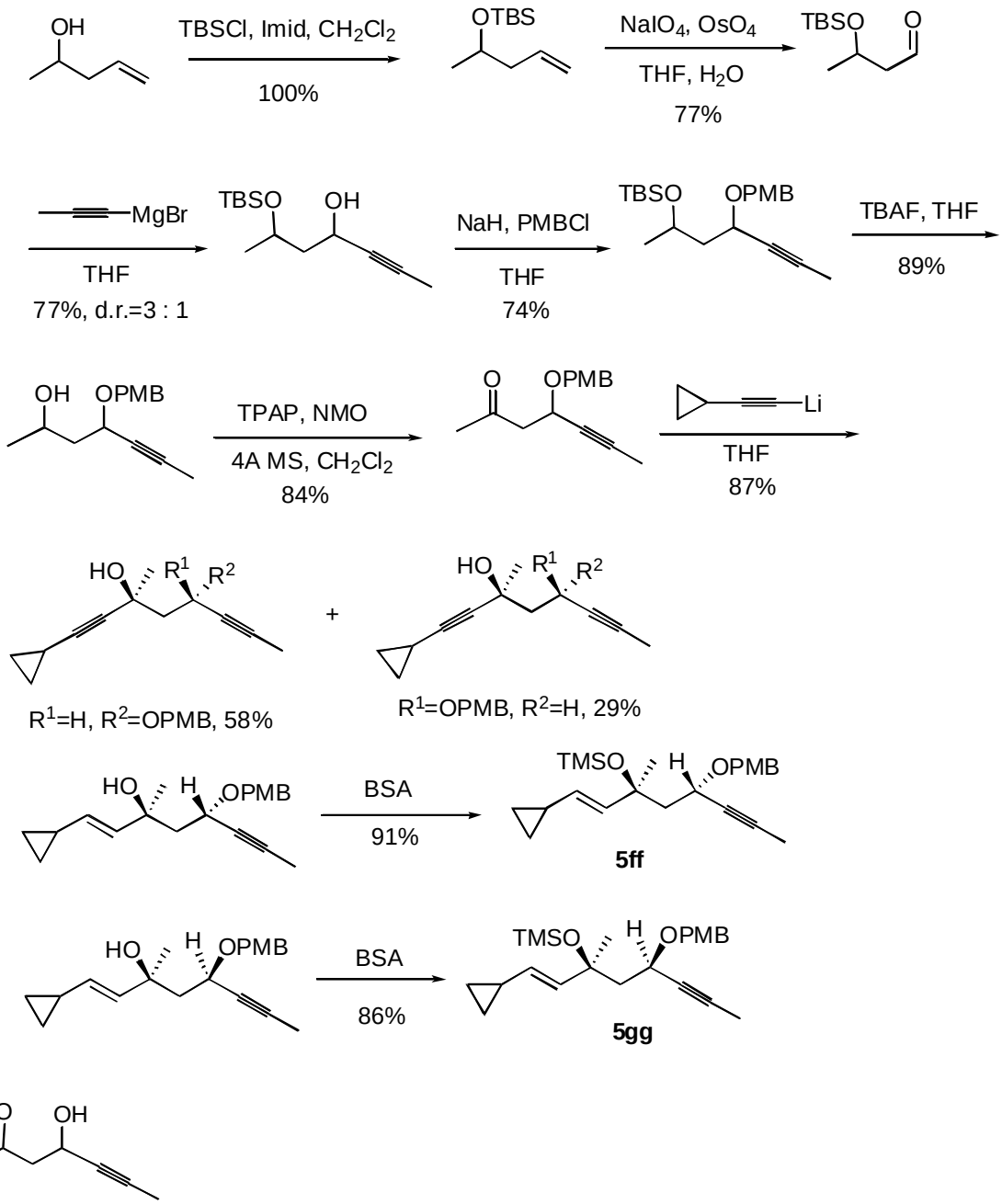
1-Cyclopropyl-1-hepten-6-yn-3-ol (5dd): To a solution of **5cc** (400 mg, 1.8 mmol) in 5 mL of THF was added TBAF (3.6 mL, 1 M in THF, 3.6 mmol) at rt. After 30 min, the mixture was concentrated in vacuo and the residue was purified by flash chromatography (15% diethyl ether in petroleum ether) to afford **5dd** (270 mg, 1.8 mmol, 100%).
IR (neat): 3375, 3303, 3062, 3006, 2925, 2868, 2117, 1666, 1430, 1100, 1049, 1021, 964, 940, 813 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.54 (dd, *J*=15.3, 7.1 Hz, 1H), 5.22 (dd, *J*=15.3, 8.8 Hz, 1H), 4.16 (q, *J*=7.1 Hz, 1H), 2.36-2.22 (m, 2H), 1.97 (t, *J*=2.7 Hz, 1H), 1.82-1.67 (m, 3H), 1.39 (m, 1H), 0.73 (m, 2H), 0.38 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 136.5, 129.5, 84.0, 71.6, 35.6, 14.7, 13.4, 6.8, 6.7. Anal. Calc'd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.14; H, 9.16.



5ee

(1*E*)-1-Cyclopropyl-5-methyl-7-(trimethylsilyl)-1-hepten-6-yne-3,5-diol (5ee): To a solution of enone (3.01 g, 12.0 mmol) in THF (60 mL) was added dropwise L-Selectride (1M in THF, 15.6 mL, 15.6 mmol) at –100 °C. After stirring for 30 min H_2O_2 (30%, 6 mL) was added and the reaction mixture warmed to rt and stirred for 1 h. The aqueous phase was extracted with diethylether (3 x 50 mL). The combined organic phases were washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by flash chromatography eluting with 33% to 50% diethyl ether in petroleum ether to afford diol **5ee** (1.49 g, 5.90 mmol, 49%, dr: 4:1) as a colorless oil, which slowly crystallized.
Mp.: < 30 °C. IR (neat): 3360bm, 2960w, 2169w, 1668w, 1411w, 1251m, 961m, 843s, 760m cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.59 (dd, *J*=7.0, 15.3 Hz, 1H), 5.22 (dd, *J*=8.9, 14.9 Hz, 1H), 4.48 (t, *J*=6.4 Hz, 1H), 3.12 (s, 1H), 2.93 (s, 1H), 2.02 (dd, *J*=9.2, 14.4 Hz, 1H), 1.83 (dd, *J*=3.4, 14.4 Hz, 1H), 1.54 (s, 3H), 1.35 (m, 1H), 0.70 (m, 2H), 0.35 (m, 2H), 0.15 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 136.1, 129.6, 109.6, 88.0, 70.0, 67.2, 48.9, 29.6, 13.3, 6.7, -0.2. Anal. Calc'd for $C_{14}H_{24}O_2Si$: Calc'd C, 66.61; H, 9.58, Found: C, 66.87; H, 9.42.

Preparation of **5ff, 5gg:**

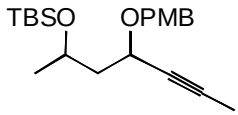


6-(*tert*-Butyldimetylsilyloxy)-hept-2-yn-4-ol: To 4-penten-2-*tert*-butyldimethyl sily ether (6.4g, 32mmol) in 200 mL of distilled THF was added osmium tetraoxide (10.2mL, 1.6mmol, 4% in water) at 0°C followed by the addition of sodium periodate (17.1g, 80mmol) in 200mL of distilled water. The solution was stirred at rt for 4 h and was diluted with 200mL of diethyl ether. The organic layer was separated and the aqueous washed with 200mL of diethyl ether. The combined organic layers were washed with saturated aqueous sodium sulfite solution. The

organic layer was dried with magnesium sulfate and concentrated in vacuo. Flash chromatography eluting with 5% diethyl ether in petroleum ether to afford aldehyde (5.0g, 24.8mmol, 77%) as slightly dark oil. To a solution of aldehyde (5.0 g, 24.8 mmol) in 40 mL of THF at -78°C was added 1-propynyl magnesium bromide (60.0 mL, 30.0 mmol, 0.5 M in THF). After 30 min, this mixture was quenched with water (30 mL) and saturated aqueous ammonium chloride (10 mL). The aqueous layer was extracted with diethyl ether (3 x 100 mL). The combined organic extracts were dried with magnesium sulfate and concentrated *in vacuo.* The residue was purified by flash chromatography eluting with 5-20% diethyl ether in petroleum ether to afford 6-(*tert*-butyldimetylsilyloxy)-hept-2-yn-4-ol (4.62 g, 19.1 mmol, d.r.=2:1, 77%) as a colorless oil.

Major diatereomer: IR (film) cm^{-1}: 3378b, 2957s, 2897s, 2858s, 2233w, 1478s, 1446m, 1372s, 1303w, 1255s, 1215w, 1187w, 1137s, 1087s, 1037s, 957se, 923m, 898s, 835s, 809s, 775s, 736w, 711w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.43 (t, 1H), 4.01 (m, 1H), 3.07 (s, 1H), 1.85 (m, 1H), 1.79 (d, J=2.0 Hz, 3H), 1.66 (ddd, J=3.5, 6.5, 13.5 Hz, 1H), 1.13 (d, J=6.5 Hz, 3H), 0.84 (s, 9H), 0.039 (s, 3H), 0.031 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 80.6, 80.1, 67.3, 61.0, 24.0, 17.7, 15.0, 3.32, -4.33, -5.12. Anal. Calc'd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 63.95; H, 10.30.

Minor diatereomer: IR (film) cm^{-1}: 3452b, 2958s, 2930s, 2889s, 2858s, 1472m, 1446m, 1377m, 1330w, 1256s, 1212w, 1154s, 1134s, 1085s, 1004s, 941w, 913w, 880w, 836s, 811s, 776s, 718w, 659w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.54 (m, 1H), 4.25 (m, 1H), 3.45 (d, J=5.5 Hz, 1H), 1.81 (d, J=3.0 Hz, 3H), 1.78 (m, 2H), 1.18 (d, J=6.0 Hz, 3H), 0.88 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 80.30, 80.29, 66.8, 60.0, 25.7, 23.3, 22.5, 3.42, -4.4, -5.0; HRMS: Calc'd for $C_{13}H_{25}O_2Si$ ($M-H^+$): 241.1624. Found: 241.1622.



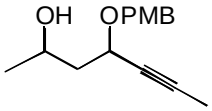
***tert*-Butyl-[3-(4-methoxy-benzyloxy)-methyl-hex-4-ynyloxy]-dimethylsilane**: To a slurry of sodium hydride (744 mg, 29.5 mmol, 95%) in 25 mL of THF at 0°C was added a solution of two diasteromers 6-(*tert*-butyldimetylsilyloxy)-hept-2-yn-4-ol (5.94 g, 24.5 mmol) in 25 mL of THF. This solution was warmed to rt over 25 min. To this solution were then added *p*-methoxybenzyl chloride (4.22 g, 3.65 mL, 27.0 mmol, freshly distilled) and sodium iodide (50 mg). The mixture was heated at reflux for 2 h. The mixture was washed with water (10 mL), dried with magnesium sulfate, concentrated *in vacuo.* The residue was purified by flash chromatography eluting with 5% to 10% diethyl ether in petroleum ether to afford *tert*-butyl-[3-(4-methoxy-benzyloxy)-methyl-hex-4-ynyloxy]-dimethylsilane (6.39 g, 17.6 mmol, 72%) as a light brown oil.

Major diatereomer: IR (film) cm^{-1}: 2956s, 2929s, 2897m, 2857s, 2342w, 1613m, 1586w, 1514s, 1464m, 1443w, 1373w, 1342w, 1302w, 1250s, 1173m, 1134m, 1094s, 1038s, 1006m, 968w, 896m, 835s, 775s, 668w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.28 (d, J=8.4 Hz, 2H), 6.86 (d, J=8.4 Hz, 2H), 4.70 (d, J=10.7 Hz, 1H), 4.44 (d, J=10.7 Hz, 1H), 4.14 (m, 1H), 4.06 (m, 1H), 3.78 (s, 3H), 1.92 (m, 1H), 1.90 (d, J=2.1 Hz, 3H), 1.13 (d, J=6.3 H, 3H), 0.84 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.1, 130.1, 129.5, 113.6, 82.0, 78.2, 69.7, 66.3, 65.6, 45.6, 25.8, 24.0, 17.9, 3.48, -4.37, -5.06.

HRMS: Calc'd for $C_{21}H_{34}O_3Si$ (M^+): 362.2277. Found: 362.2275.

For minor diatereomer:

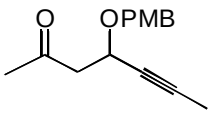
IR (film) cm^{-1}: 2956s, 2929s, 2897m, 2857s, 2342w, 1613m, 1586w, 1514s, 1464m, 1443w, 1373w, 1342w, 1302w, 1250s, 1173m, 1134m, 1094s, 1038s, 1006m, 968w, 896m, 835s, 775s, 668w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.28 (d, J=8.4 Hz, 2H), 6.86 (d, J=8.4 Hz, 2H), 4.71 (d, J=10.7 Hz, 1H), 4.43 (d, J=10.7 Hz, 1H), 4.14 (m, 1H), 4.06 (m, 1H), 3.78 (s, 3H), 1.92 (m, 1H), 1.90 (d, J=2.1 Hz, 3H), 1.13 (d, J=6.3 H, 3H), 0.89 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 130.4, 129.9, 114.1, 114.0, 82.5, 78.7, 70.0, 65.8, 64.7, 46.6, 25.7, 24.1, 15.2, 3.48, -4.28, -4.90; HRMS: Calc'd for $C_{17}H_{25}O_3Si$ $(M\text{-}C_4H_9)^+$: 305.1573. Found: 305.1582.



4-(4-Methoxybenzyloxy)-hept-5-yn-2-ol: To a solution of *tert*-butyl-[3-(4-methoxy-benzyloxy)-methyl-hex-4-ynyloxy]-dimethylsilane (600 mg, 1.66 mmol) in 2 mL of THF was added TBAF (3.3 mL, 3.3 mmol, 1 M in THF) at rt. This mixture was stirred overnight. Without workup, the mixture was purified by flash chromatography eluting with 5% to 25% diethyl ether in petroleum ether to afford alcohol 4-(4-methoxybenzyloxy)-hept-5-yn-2-ol (490 mg, 1.66 mmol, 100%) as a colorless oil.

Major diastereomer: IR (film) cm^{-1}: 3450b, 2986m, 2922m, 2866m, 1613s, 1586m, 1514s, 1460m, 1375m, 1302s, 1249s, 1174m, 1072s, 1035s, 944w, 822m; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.23 (d, J=8.4 Hz, 2H), 6.82 (d, J=8.4 Hz, 2H), 4.70 (d, J=11.4 Hz, 1H), 4.39 (d, J=11.4 Hz, 1H), 4.20 (m, 1H), 3.93 (m, 1H), 3.74 (s, 3H), 3.26 (bs, 1H), 1.87 (m, 1H), 1.75 (m, 1H), 1.85 (d, J=2.1 Hz, 3H), 1.11 (d, J=3.3 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.1, 129.5, 129.4, 113.6, 82.3, 77.4, 69.9, 67.9, 66.4, 55.0, 44.5, 25.5, 23.1.

Minor diastereomer: IR (film) cm^{-1}: 3450b, 2986m, 2922m, 2866m, 1613s, 1586m, 1514s, 1460m, 1375m, 1302s, 1249s, 1174m, 1072s, 1035s, 944w, 822m; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.23 (d, J=8.4 Hz, 2H), 6.82 (d, J=8.4 Hz, 2H), 4.69 (d, J=11.4 Hz, 1H), 4.38 (d, J=11.4 Hz, 1H), 4.30 (m, 2H), 3.74 (s, 3H), 3.26 (bs, 1H), 1.87 (m, 1H), 1.75 (m, 1H), 1.85 (d, J=2.1 Hz, 3H), 1.10 (d, J=3.3 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.2, 133.3, 128.4, 113.7, 82.6, 70.1, 66.8, 64.8, 64.5, 53.6, 43.8, 23.1, 20.7; HRMS: Calc'd for $C_{15}H_{20}O_3$ (M^+): 248.1412. Found: 248.1414.

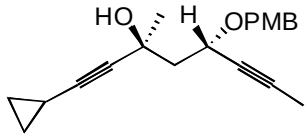


4-(4-Methoxybenzyloxy)-hept-5-yn-2-one: To 4-(4-methoxybenzyloxy)-hept-5-yn-2-ol (480 mg, 1.94 mmol) in 3 mL of dichloromethane at 0°C were added NMO (325 mg, 2.90 mmol), 4A molecular sieves (650 mg) and TPAP (27 mg, 0.078 mmol). After stirring at rt for 15 min at 0°C, the mixture was warmed to rt. After 3 h, the mixture was directly purified by flash chromatography eluting with 25% diethyl ether in petroleum ether to afford 4-(4-methoxybenzyloxy)-hept-5-yn-2-one (306 mg, 1.24 mmol) as a pale yellow oil.

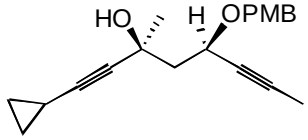
IR (film) cm^{-1}: 3001m, 2921s, 2858s, 2868s, 2236w, 1716s, 1613s, 1588w, 1514s, 1464m, 1443m, 1382s, 1302s, 1249s, 1174s, 1141m, 1086s, 1034s, 823m; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.22 (d, J=8.6 Hz, 2H), 6.85 (d, J=8.6 Hz, 2H), 4.66 (d, J=11.0 Hz, 1H), 4.50 (m, 1H), 4.37 (d, J=11.0 Hz, 1H), 3.74 (s, 3H), 2.90 (dd, J=7.8, 16.0 Hz, 1H), 2.70 (dd, J=5.4, 16.2 Hz), 2.10 (s, 3H), 1.83 (d, J=2.0 Hz, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ 205.3, 159.1, 129.6, 129.5, 113.6,

82.2, 70.1, 64.3, 49.5, 30.4, 25.4, 3.23; HRMS: Calc'd for $C_{15}H_{18}O_3$ (M^+): 246.1256. Found: 246.1254.

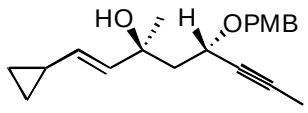
To cyclopropylacetylene (297 mg, 4.5 mmol) in 10 mL of distilled THF was added *n*-butyllithium (3.0 mL, 4.8 mmol, 1.6M in hexanes) at –78°C. After 30 min, to this dark brown solution was added a solution of 4-(4-methoxybenzyloxy)-hept-5-yn-2-one (1.07 g, 4.34 mmol) in 5 mL of distilled THF at –78°C very slowly in 5 min. The reaction mixture was warmed to rt overnight. The mixture was then quenched with 10 mL of water. The aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were concentrated *in vacuo* and submitted to silica gel chromatography eluting with 5% to 15% diethyl ether in petroleum ether to afford two diastereomers (3*S**,5*S**)-1-cyclopropyl-5-(4-methoxybenzyloxy)-3-methyl-octa-1,6-diyn-3-ol (786 mg, 2.52 mmol, 58%) and (3*S**,5*R**)-1-cyclopropyl-5-(4-methoxybenzyloxy)-3-methyl-octa-1,6-diyn-3-ol (393 mg, 1.26 mmol, 29%).



(3*S,5*S**)-1-Cyclopropyl-5-(4-methoxybenzyloxy)-3-methyl-octa-1,6-diyn-3-ol**: IR (film) cm^{-1}: 3494bs, 2980s, 2933s, 2868s, 2837m, 2232m, 1613s, 1586m, 1515s, 1465m, 1401s, 1370m, 1332m, 1303s, 1249s, 1175s, 1091s, 1031s, 935w, 908w, 822s, 759w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.33 (dd, J=2.5, 6.5 Hz, 2H), 6.91 (dd, J=2.0, 6.5 Hz, 2H), 4.78 (d, J=11.0 Hz, 1H), 4.69 (dm, J=2.0, 11.5 Hz, 1H), 4.49 (d, J=11.0 Hz, 1H), 4.48 (s, 1H), 3.82 (s, 3H), 2.14 (dd, J=11.0, 14.5 Hz, 1H), 1.93 (m, 1H), 1.92 (d, J=2.0 Hz, 3H), 1.42 (d, J=0.5 Hz, 3H), 1.18 (m, 1H), 0.73 (m, 2H), 0.58 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.4, 130.0, 129.1, 113.8, 87.3, 82.5, 77.9, 70.6, 68.0, 67.4, 55.2, 48.1, 30.5, 8.25, 8.21, 3.60, -0.68. Anal. Calc'd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.85; H, 7.80.



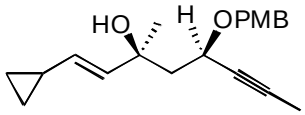
(3*S,5*R**)-1-Cyclopropyl-5-(4-methoxybenzyloxy)-3-methyl-octa-1,6-diyn-3-ol**: IR (film) cm^{-1}: 3493b, 2932m, 2837w, 2238w, 1613s, 1585w, 1513s, 1464m, 1360w, 1302m, 1249s, 1176s, 1096m, 1034s, 822m; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.28 (dd, J=2.1, 9.0 Hz, 2H), 6.87 (dd, J=2.1, 9.6 Hz, 2H), 4.72 (d, J=11.4 Hz, 1H), 4.44 (d, J=11.4 Hz, 1H), 4.39 (m, 1H), 3.80 (s, 3H), 2.21 (dd, J=7.5, 14.4 Hz, 1H), 2.02 (dd, J=9.0, 14.4 Hz, 1H), 1.90 (d, J=2.1 Hz, 3H), 1.4 1 (s, 3H), 1.19 (m, 1H), 0.71 (m, 2H), 0.59 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.3, 129.8, 129.5, 113.8, 100.2, 86.9, 83.7, 78.5, 77.9, 69.8, 66.7, 65.9, 55.2, 48.2, 30.0, 8.16, 3.63, -0.68; HRMS: Calc'd for $C_{20}H_{24}O_3$: 312.1725. Found: 312.1728.



(3*S,5*S**)-1-Cyclopropyl-5-(4-methoxybenzyloxy)-3-methyl-octa-1-en-6-yn-3-ol**: To a solution of (3*S**,5*S**)-1-cyclopropyl-5-(4-methoxybenzyloxy)-3-methyl-octa-1,6-diyn-3-ol (1.46

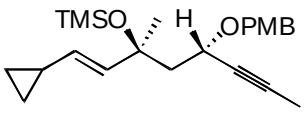
g, 4.68 mmol) in THF (10 mL) at 0ºC was added Red-Al (3.64 g, 3.51 mL, 11.7 mmol, 65% in toluene). The reaction mixture was warmed to rt for 3 h. The reaction mixture at 0°C was quenched with a saturated aqueous solution of Rochelle's salt (10 mL). The aqueous fraction was extracted with diethyl ether (3 x 100 mL). The combined organic extracts were dried with magnesium sulfate and concentrated *in vacuo*. The residue was purified by flash chromatography eluting with 5% to 30% diethyl ether in petroleum ether to afford (3*S**,5*S**)-1-cyclopropyl-5-(4-methoxybenzyloxy)-3-methyl-octa-1-en-6-yn-3-ol (1.35g, 4.30 mmol, 91%) as a pale yellow oil.

IR (film) cm^{-1}: 3501bs, 3080w, 3003m, 2969s, 2921s, 2867m, 2231w, 1666w, 1613s, 1514s, 1456m, 1443m, 1423w, 1398m, 1367m, 1330m, 1302s, 1250s, 1174s, 1140m, 1090s, 1034s, 968m, 935w, 821s, 758w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.28 (dd, J=2.5, 8.0 Hz, 2H), 6.89 (dd, J=2.0, 7.5Hz, 2H), 5.45 (d, J=15.5 Hz, 1H), 5.16 (dd, J=4.0, 15.5 Hz, 1H), 4.72 (d, J=11.0 Hz, 1H), 4.37 (d, J=11.0 Hz, 1H), 4.31 (dt, J=2.0, 11.0 Hz, 1H), 3.99 (s, 1H), 3.81 (d, J=2.0 Hz, 3H), 2.13 (dd, J=10. 5, 15.0 Hz, 1H), 1.90 (t, J=1.5 Hz, 3H), 1.81 (dd, J=2.5, 14.5 Hz, 1H), 1.35 (m, 1H), 1.19 (d, J=2.5 Hz, 3H), 1.35 (m, 1H), 0.68 (m, 2H), 0.32 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.3, 132.9, 132.4, 129.8, 129.1, 113.7, 82.2, 77.5, 72.3, 70.2, 67.0, 55.1, 47.0, 29.6, 13.2, 6.61, 6.56, 3.46; HRMS: Calc'd for $C_{20}H_{26}O_3$: 314.1882. Found: 314.1885.



(3*S,5*R**)-1-Cyclopropyl-5-(4-methoxybenzyloxy)-3-methyl-octa-1-en-6-yn-3-ol**: To a solution of (3*S**,5*R**)-1-cyclopropyl-5-(4-methoxybenzyloxy)-3-methyl-octa-1,6-diyn-3-ol (0.62 g, 4.68 mmol) in THF (5 mL) at 0ºC was added Red-Al (1.68 g, 1.62 mL, 4.98 mmol, 65% in toluene). The reaction mixture was warmed to rt for 3h. The reaction mixture at 0°C was quenched with a saturated aqueous solution of Rochelle's salt (10 mL). The aqueous fraction was extracted with diethyl ether (3 x 100 mL). The combined organic extracts were dried with magnesium sulfate and concentrated *in vacuo*. The residue was purified by flash chromatography eluting with 5% to 30% diethyl ether in petroleum ether to afford (3*S**,5*R**)-1-cyclopropyl-5-(4-methoxybenzyloxy)-3-methyl-octa-1-en-6-yn-3-ol (0.54 g, 1.71 mmol, 86%) as a pale yellow oil.

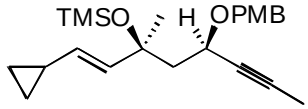
IR (film) cm^{-1}: 3508b, 3078w, 3006w, 2961w, 2921m, 2861w, 2361m, 1665w, 1612m, 1586w, 1514s, 1462m, 1302m, 1249s, 1175s, 1070s, 1035s, 965s, 822m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.31 (dd, J=3.0, 11.0 Hz, 2H), 6.89 (dd, J=2.0 Hz, 8.5 Hz, 2H), 5.57 (d, J=15.5 Hz, 1H), 5.17 (dd, J=8.5, 15.0 Hz, 1H), 4.74 (d, J=11.0 Hz, 1H), 4.44 (d, J=11.5 Hz, 1H), 4.33 (m, 1H), 3.82 (s, 3H), 2.07 (dd, J=4.0, 15.0 Hz, 1H), 1.92 (d, J=2.0 Hz, 3H), 1.88 (dd, J=4.5, 14.5 Hz, 1H), 1.37 (m, 1H), 1.20 (s, 3H), 0.70 (m, 2H), 0.37 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.3, 134.3, 131.5, 129.9, 129.3, 113.8, 82.8, 77.8, 71.6, 70.1, 66.1, 55.2, 47.2, 27.4, 13.4, 6.62, 3.59, -11.8; HRMS: Calc'd for $C_{20}H_{26}O_3$: 314.1882. Found: 314.1882.



5ff

(1*S,3*S**)-[1-(2-Cyclopropylvinyl)-3-(4-methoxybenzyloxy)-1-methyl-hex-4-ynyl-oxy]-trimethylsilane** (**5ff**): To alcohol (3*S**,5*S**)-1-cyclopropyl-5-(4-methoxybenzyloxy)-3-methyl-

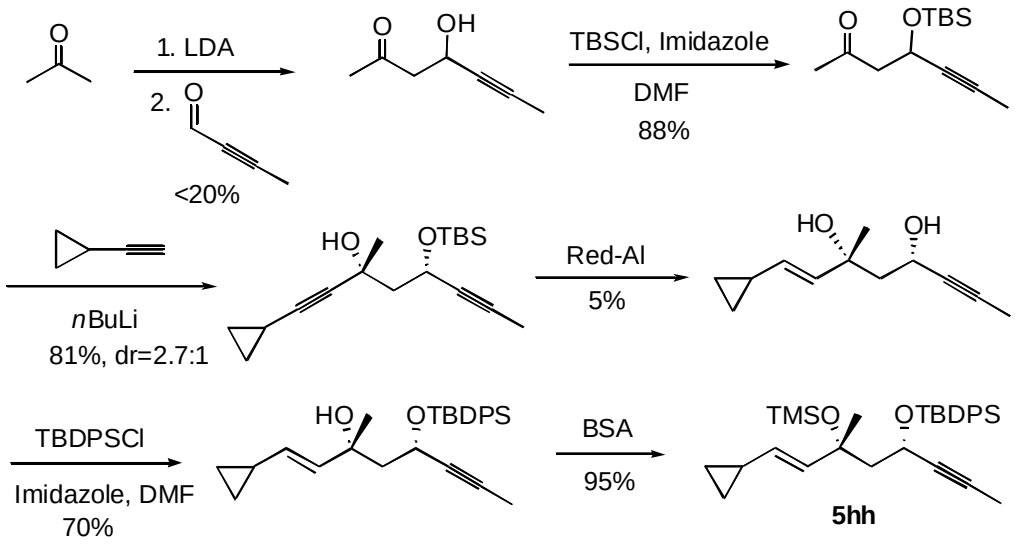
octa-1-en-6-yn-3-ol (1.35 g, 4.30 mmol) was added BSA (3.5 mL, 2.88 g, 14.2 mmol, freshly distilled) at rt. The initial reaction was exothermic but no cooling bath is required. The reaction mixture was stirred at rt for 24 h at which time the reaction was complete. To the reaction mixture in an ice bath was added a slurry of silica gel in petroleum ether to quench the BSA (otherwise during loading a lot of heat was generated). The whole mixture was then separated by flash chromatography eluting with pure petroleum ether and then 5% diethyl ether in petroleum ether to afford the TMS ether **5ff** in 91% yield (1.51g, 3.9 mmol).
IR (film) cm^{-1}: 2957s, 2863m, 1613m, 1587m, 1514s, 1466m ,1302m, 1249s, 1173m, 1101s, 1039s, 967w, 841s, 755w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.31 (dd, J=2.5, 9.0 Hz, 2H), 6.89 (d, J=8.0 Hz, 2H), 5.60 (d, J=15.5 Hz, 1H), 5.07 (dd, J=8.5, 15.0 Hz, 1H), 4.69 (d, J=11.0 Hz, 1H), 4.41 (d, J=11.5 Hz, 1H), 4.24 (m, 1H), 3.82 (s, 3H), 1.98 (d, J=5.5 Hz, 2H), 1.90 (d, J=1.5 Hz, 3H), 1.33 (s, 3H), 0.69 (m, 2H), 0.90 (m, 1H), 0.35 (m, 2H), 0.08 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 150.0, 135.1, 131.3, 130.4, 129.6, 113.6, 79.5, 74.1, 69.8, 65.6, 55.2, 50.1, 27.6, 13.3, 6.41, 6.37, 3.56, 2.51, 1.80; HRMS: Calc'd for $C_{22}H_{31}O_3Si$ ($M-CH_3^+$): 371.2042. Found: 371.2045.

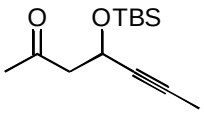


5gg

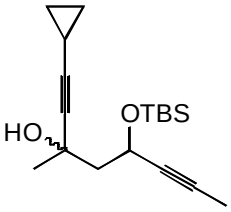
(1*S,3*R**)-[1-(2-Cyclopropyl-vinyl)-3-(4-methoxybenzyloxy)-1-methyl-hex-4-ynyl-oxy]-trimethylsilane** (**5gg**): To (3*S**,5*R**)-1-cyclopropyl-5-(4-methoxybenzyloxy)-3-methyl-octa-1-en-6-yn-3-ol (0.54 g, 1.71 mmol) was added BSA (1.0 mL, freshly distilled) at rt. The reaction mixture was stirred at rt for 24 h. To the reaction mixture in an ice bath was added a slurry of silica gel in petroleum ether to quench the BSA (otherwise during loading a lot of heat was generated). The whole mixture was then separated by flash chromatography eluting with pure petroleum ether and then 5% diethyl ether in petroleum ether to afford the TMS ether **5gg** as a colorless oil (0.63 g, 1.63 mmol, 91%).
IR (film) cm^{-1}: 3082w, 2956s, 2865m, 1684w, 1613m, 1586w, 1514s, 1458m, 1302m, 1249s, 1173m, 1094s, 1039s, 966m, 840s, 755m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.32 (d, J=8.5 Hz, 2H), 6.88 (d, J=8.5 Hz, 2H), 5.58 (d, J=16.0 Hz, 1H), 5.03 (dd, J=8.5, 15.0 Hz, 1H), 4.67 (d, J=11.0 Hz, 1H), 4.38 (d, J=11.0 Hz, 1H), 4.18 (m, 1H), 3.82 (s, 3H), 2.03 (dd, J=6.5, 13.0 Hz, 1H), 1.98 (dd, J=4.5, 13.0 Hz, 1H), 1.89 (d, J=2.0 Hz, 3H), 1.35 (m, 1H), 1.34 (s, 3H), 0.70 (s, 2H), 0.33 (s, 2H), 0.097 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.0, 134.5, 131.5, 130.4, 129.6, 113.6, 81.1, 79.5, 74.4, 69.7, 65.6, 55.2, 50.4, 28.2, 13.4, 6.47, 6.44, 3.64, 2.50; HRMS: Calc'd for $C_{22}H_{31}O_3Si$ ($M-CH_3^+$): 371.2042. Found: 371.2043.

5hh:



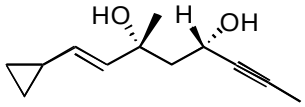


4-*tert*-Butyldimethylsilyloxy-5-heptyn-2-one: To 4-hydroxy-5-heptyn-2-one (0.27 g, 2.14 mmol) in 5 mL of distilled dichloromethane was added imidazole (306 mg, 4.49 mmol) followed by the addition of tert-butyldimethyl silyl chloride (0.35 g, 2.35 mmol) at rt. After 2h, flash chromatography of the reaction mixture eluting with 10% to 50% diethyl ether in petroleum ether afforded 4-*tert*-butyldimethylsilyloxy-5-heptyn-2-one (0.45 g, 1.88 mmol, 88%).
^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.78 (m, 1H), 2.85 (dd, J=8.0, 15.5 Hz, 1H), 2.65 (dd, J=5.0, 15.5 Hz, 1H), 2.18 (s, 3H), 1.82 (s, 3H), 0.88 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H).

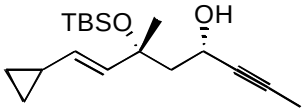


5-*tert*-Butyldimethylsilyloxy-1-cyclopropyl-3-methylhepta-1,6-diyn-3-ol: To a solution of cyclopropylacetylene (66 mg, 2.4 mmol) in 2 mL of THF was added *n*BuLi (0.47 mL, 0.67 mmol, 1.6 M in hexane) at -78^{o}C. After 30 min, to this solution was added a solution of 4-*tert*-butyldimethylsilyloxy-5-heptyn-2-one (100 mg, 0.42 mmol) in 2 mL of THF. The resulting solution was slowly warmed to rt over 1h and quenched with water. After separation of the organic layer, the aqueous layer was extracted with diethyl ether (3 x 15 mL). The combined organic fractions were dried with magnesium sulphate and concentrated *in vacuo*. The residue was purified by flash chromatography eluting with 5% to 15% of diethyl ether in petroleum ether to give 5-*tert*-butyldimethylsilyloxy-1-cyclopropyl-3-methylhepta-1,6-diyn-3-ol as a mixture of two diastereomers (104 mg, 0.34 mmol, 81%, d.r.=2.7:1).
For major diastereomer: IR (film) cm^{-1}: 3501bs, 2956s, 2931s, 2886m, 2859s, 2233w, 1722w, 1472m, 1390m, 1362m, 1258s, 1177w, 1159s, 1092s, 1056m, 1028w, 1001s, 947m, 924w, 937s, 885m, 812s, 781s, 723w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.97 (m, 1H), 4.70 (s, 1H), 2.05 (dd,

J=11.0, 14.0 Hz, 1H), 1.84 (dt, J=2.5, 10.0 Hz, 1H), 1.83 (d, J=2.0 Hz, 3H), 1.41 (s, 3H), 1.24 (m, 1H), 0.93 (s, 9H), 0.76 (m, 2H), 0.65 (m, 2H), 0.23 (s, 3H), 0.22 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 87.3, 81.5, 80.0, 78.0, 67.5, 62.9, 49.4, 30.6, 25.7, 17.9, 8.1, 8.0, 3.38, -0.67, -4.14, -5.19; For minor diastereomer: IR (film) cm^{-1}: 3451b, 3013w, 2957s, 2930s, 2886w, 2858m, 2237w, 1473w, 1464w, 1390w, 1255s, 1175w, 1153w, 1096s, 1028w, 1005w, 930m, 882m, 838s, 812m, 778s; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.75 (m, 1H), 3.78 (s, 1H), 2.12 (dd, J=7.0, 14.5 Hz, 1H), 2.01 (dd, J=7.0, 14.0 Hz, 1H), 1.86 (d, J=2.0 Hz, 3H), 1.48 (s, 3H), 1.26 (m, 1H), 0.92 (s, 9H), 0.77 (m, 2H), 0.68 (m, 2H), 0.18 (s, 3H), 0.17 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 86.9, 82.6, 80.6, 78.5, 66.6, 61.1, 50.2, 30.1, 25.8, 18.1, 8.18, 8.17, 3.54, -0.64, -4.35, -5.04.



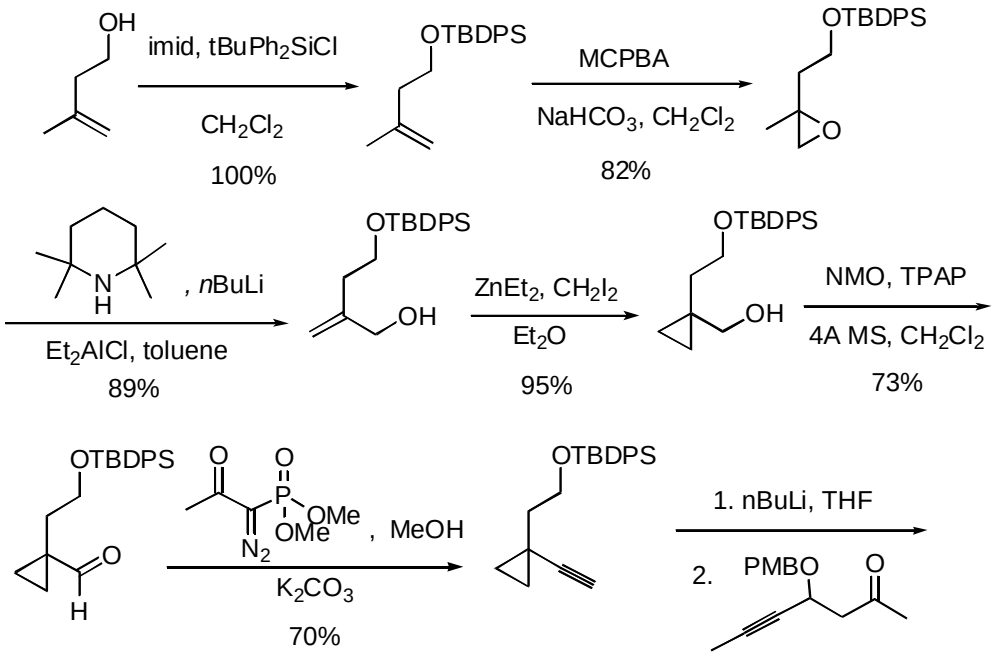
***syn-E*-1-Cyclopropyl-3-methyl-oct-1-en-6-yn-3,5-diol**: To a solution of *syn-E*-5-*tert*-butyldimethylsilyloxy-1-cyclopropyl-3-methylhepta-1,6-diyn-3-ol (470 mg, 1.5 mmol) in 5 mL of THF was added Red-Al (65%wt in toluene, 340 mg, 1.7 mmol) at –78 °C. After 10 min, the solution was warmed to -15 °C and stirred at this temperature for additional 1h. Afterwards it was recooled to –78 °C before it was quenched with water. The solution was then warmed to rt and submitted to flash chromatography eluting with 10%-40% ether in petroleum ether without further work-up. *syn-E*-1-cyclopropyl-3-methyl-oct-1-en-6-yn-3,5-diol (29 mg, 0.15 mmol, 10%) was obtained accompanied with the starting material and other impurities.
IR (film) cm^{-1}: 3356, 3082, 2973, 2921, 2231, 1666, 1428, 1374, 1091, 1049; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.63 (d, J=15.6 Hz, 1H), 5.17 (dd, J=8.8, 15.6 Hz, 1H), 4.67 (m, 1H), 3.19 (d, *J*=3.2 Hz, 1H), 2.65 (s, 1H), 2.00 (dd, J=9.6, 14.4 Hz, 1H), 1.81 (m, 1H), 1.83 (s, 3H), 1.38 (m, 1H), 1.33 (s, 3H), 0.70 (m, 2H), 0.36 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 134.4, 132.2, 81.3, 80.1, 72.6, 60.1, 48.3, 27.2, 13.4, 6.7, 3.5.

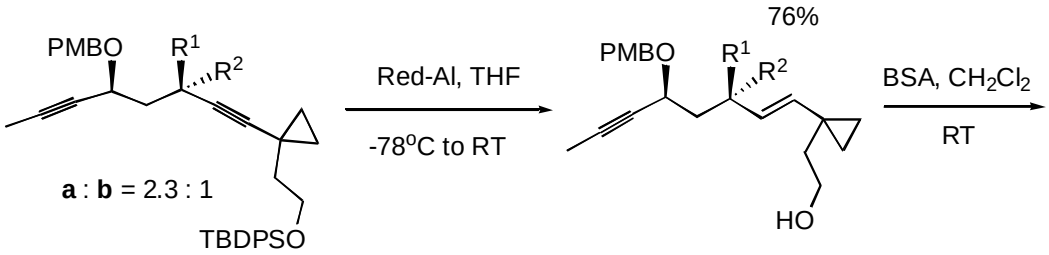


***syn-E*-5-(*tert*-Butyldiphenylsilyloxy)-1-cyclopropyl-3-methyl-oct-1-en-6-yn-3-ol:** To a solution of *syn-E*-1-cyclopropyl-3-methyl-oct-1-en-6-yn-3,5-diol (762 mg, 3.92 mmol) in 5 mL of DMF was added imidazole (560 mg, 8.23 mmol) and TBDPSCl (1.19 g, 4.33 mmol). The mixture was stirred for 2h and poured into water (20 mL). The mixture was then extracted with diethyl ether (3 x 30 mL), washed with brine (50 mL) and the organic layers were dried with magnesium sulfate. After the removal of solvent *in vacuo*, the residue was purified by flash chromatography using 1/9 of diethyl ether in petroleum ether to give *syn-E*-5-(*tert*-butyldiphenylsilyloxy)-1-cyclopropyl-3-methyl-oct-1-en-6-yn-3-ol (1.19 g, 2.75 mmol, 70%). To *syn-E*-5-(*tert*-butyldiphenylsilyloxy)-1-cyclopropyl-3-methyl-oct-1-en-6-yn-3-ol (0.54 g, 1.71 mmol) was added BSA (1.0 mL, freshly distilled, old BSA at rt. The reaction mixture was stirred at rt for 24 h and came to completion. The initial reaction was exothermic but no cooling bath is required. To the reaction mixture was added silica gel slurry in petroleum ether to quench the BSA in ice-bath(otherwise during loading event a lot of heat was generated). The whole

mixture was then separated by flash chromatography eluting with pure petroleum ether and then 5% diethyl ether in petroleum ether to afford **5hh** (0.82 g, 1.62 mmol, 95%).
For *syn-E*-5-(*tert*-butyldiphenylsilyloxy)-1-cyclopropyl-3-methyl-oct-1-en-6-yn-3-ol: IR (film) cm^{-1}: 3513, 2960, 2858, 2239, 1666, 1113, 1061, 965, 822 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.77-7.71 (m, 4H), 7.45-7.35 (m, 6H), 5.43 (d, *J*=15.4 Hz, 1H), 5.16 (dd, *J*=8.5, 15.4 Hz, 1H), 4.53 (m, 1H), 3.64 (s, 1H), 1.94 (m, 2H), 1.50 (s, 3H), 1.35-1.20 (m, 1H), 1.24 (s, 3H), 1.04 (s, 9H), 0.65 (m, 2H), 0.32 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 136.0, 135.8, 134.8, 134.0, 133.5, 133.0, 131.4, 129.8, 129.6, 129.4, 127.7, 127.6, 127.1, 83.9, 80.4, 71.8, 62.2, 49.0, 28.3, 26.9, 26.5, 19.1, 13.4, 6.6, 3.3. Anal. Calc'd for $C_{28}H_{36}O_2Si$: C, 77.73; H, 8.39. Found: C, 77.77; H, 8.31.

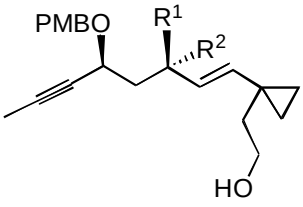
5ii, 5jj:



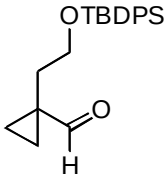


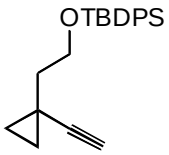
a: R^1=Me, R^2=OH
b: R^1=OH, R^2=Me

a: R^1=Me, R^2=OH, 81%
b: R^1=OH, R^2=Me, 84%

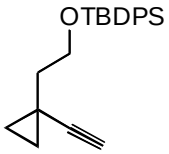


5ii: R^1=Me, R^2=OTMS, 88%
5jj: R^1=OTMS, R^2=Me, 89%





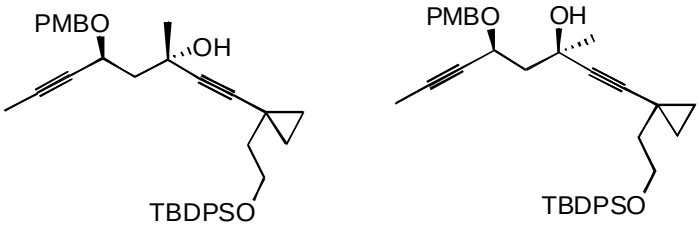
1-[2-(*tert*-Butyldiphenylsilyloxy)-ethyl]-cyclopropanecarboxaldehyde: Method A: To alcohol (288 mg, 0.81 mmol) prepared according to the literature preparation[31] in 3 mL of dichloromethane was added 300 mg of powdered 4A molecular sieves and NMO (136 mg, 1.22 mmol) at 0°C and the resulting solution was stirred at rt for 30 min. To this mixture was added TPAP (11 mg, 0.0324 mmol) at 0°C. The mixture was stirred at 0°C before it was warmed to rt. The reaction mixture was stirred at rt for 3 h and without workup, directly chromatographed eluting with 5% to 15% diethyl ether in petroleum ether to afford 1-[2-(*tert*-butyldiphenylsilyloxy)-ethyl]-cyclopropanecarboxaldehyde (208 mg, 0.59 mmol, 73%) as a pale yellow oil.
Method B: To alcohol (139 mg, 0.367 mmol) in 2 mL of distilled dichloromethane in the presence of 4Å molecular sieves was added PCC (158 mg, 0.733 mmol) at 0°C. The resulting dark brown mixture was stirred for 30 min at this temperature and then warmed to rt and stirred for an additional 2h. The reaction mixture was then chromatographed eluting with 5% to 20% diethyl ether in petroleum ether without further work-up to afford 1-[2-(*tert*-butyldiphenylsilyloxy)-ethyl]-cyclopropanecarboxaldehyde (112 mg, 0.319 mmol, 87%) as a pale yellow oil.
IR (film) cm^{-1}: 3072w, 2959m, 2931s, 2858s, 2732w, 1712s, 1472w, 1428m, 1112s, 903w, 822m, 739m, 702s; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.87 (s, 1H), 7.68 (m, 4H), 7.40 (m, 6H), 3.80 (t, J=6.6 Hz, 2H), 1.92 (t, J=6.6 Hz, 2H), 1.18 (m, 2H), 1.07 (s, 9H), 0.95 (m, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ 202.1, 135.6, 134.8, 133.7, 129.6, 127.7, 33.4, 29.6, 26.7, 26.5, 19.0. Anal. Calc'd for $C_{22}H_{28}O_2Si$: C, 74.95; H, 8.00. Found: C, 74.77; H, 7.88.



***tert*-Butyl-[2-(1-ethynylcyclopropyl)-ethoxy]-diphenylsilane:** To 1-[2-(*tert*-butyldiphenylsilyloxy)-ethyl]-cyclopropanecarboxaldehyde (200 mg, 0.57 mmol) in 2 mL of distilled methanol was added potassium carbonate (157 mg, 1.14 mmol) followed by the addition of diazo 2-oxo-propyl dimethylphosphonate (131 mg, 0.68 mmol) in 1 mL of methanol at rt. The reaction mixture was stirred at rt overnight. Without further work-up the mixture was submitted to silica gel column chromatography eluting with 5% diethyl ether in petroleum ether to afford *tert*-butyl-[2-(1-ethynylcyclopropyl)-ethoxy]-diphenylsilane (139 mg, 0.40 mmol, 70%) as a colorless oil.
IR (film) cm^{-1}: 3312m, 3071m, 3050m, 3013m, 2932s, 2858s, 2112w, 1959w, 1889w, 1823w, 1590w, 1472m, 1428s, 1390m, 1362w, 1258w, 1190w, 1111s, 1027m, 998m, 959m, 938m, 918w, 865w, 823s, 739s, 702s, 648m; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.75 (m, 4H), 7.43 (m, 6H), 3.95 (t, J=6.6 Hz, 2H), 1.81 (s, 1H), 1.65 (t, J=6.6 Hz, 2H), 1.11 (s, 9H), 0.91 (m, 2H), 0.66

[31] a. Meyers, A.; Dragovich, P. S.; Kuo, E. Y. *J. Am. Chem. Soc.* **1992**, *114*, 9369. b. Weigand, S.; Bruckner, R. *Synlett.* **1996**, 475.

(m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 135.6, 133.9, 129.5, 127.6, 88.9, 64.5, 62.4, 40.4, 26.8, 19.1, 14.9, 8.72. Anal. Calc'd for $C_{23}H_{28}OSi$: C, 79.26; H, 8.10. Found: C, 78.98; H, 8.01.



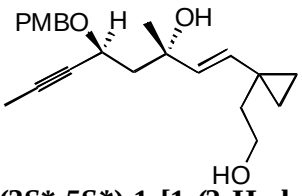
(3*S,5*S**)-1-{1-[2-(*tert*-Butyldiphenylsilyloxy)-ethyl]-cyclopropyl}-5-(4-methoxyben-zyl-oxy)-3-methyl-octa-1,6-diyn-3-ol** and **(3*R**, 5*S**)-1-{1-[2-(*tert*-Butyldiphenylsilyloxy)-ethyl]-cyclopropyl}-5-(4-methoxybenzyloxy)-3-methyl-octa-1,6-diyn-3-ol**: To *tert*-butyl-[2-(1-ethynylcyclopropyl)-ethoxy]-diphenylsilane (1.20 g, 3.45 mmol) in 20 mL of distilled THF was added *n*-butyllithium (2.4 mL, 3.78 mmol, 1.6M in hexanes) at −78°C. After 30 min, to this dark brown solution was added 4-(4-methoxybenzyloxy)-hept-5-yn-2-one (851 mg, 3.46 mmol) in 10 mL of distilled THF at −78°C very slowly in 5 min. The reaction mixture was warmed to rt overnight. The mixture was then quenched with 10 mL of water. The aqueous layer was extracted with diethyl ether (3 x 50 m). The combined organic layers were concentrated *in vacuo* and submitted to silica gel chromatography eluting with 5% to 15% diethyl ether in petroleum ether to afford two diastereomers (3*S**,5*S**)-1-{1-[2-(*tert*-butyldiphenylsilyloxy)-ethyl]-cyclopropyl}-5-(4-methoxyben-zyl-oxy)-3-methyl-octa-1,6-diyn-3-ol and (3*R**,5*S**)-1-{1-[2-(*tert*-butyldiphenylsilyloxy)-ethyl]-cyclopropyl}-5-(4-methoxyben-zyl-oxy)-3-methyl-octa-1,6-diyn-3-ol **(**1.55 g, 2.61 mmol, 76%, 2.3:1) as yellow oils.

Major isomer (3*S**,5*S**)-1-{1-[2-(*tert*-butyldiphenylsilyloxy)-ethyl]-cyclopropyl}-5-(4-methoxyben-zyl-oxy)-3-methyl-octa-1,6-diyn-3-ol (less polar):

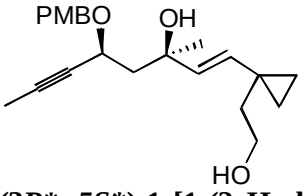
IR (film) cm^{-1}: 3501b, 3072m, 3049m, 2932s, 2858s, 2228w, 2065w, 1960w, 1889w, 1829w, 1774w, 1613s, 1588m, 1515s, 1472m, 1428s, 1393m, 1335m, 1303m, 1251s, 1210w, 1174s, 1159s, 1111s, 1030s, 959w, 935w, 911w, 823s, 738s, 703s; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.70 (m, 4H), 7.40 (m, 6H), 7.24 (d, J=8.7 Hz, 2H), 6.84 (d, J=8.7 Hz, 2H), 4.70 (d, J=9.0 Hz, 1H), 4.60 (dm, J=10.5 Hz, 1H), 4.37 (s, 1H), 4.34 (d, J=8.7 Hz, 1H), 3.86 (t, J=7.2 Hz, 2H), 3.77 (s, 3H), 2.10 (dd, J=11.4, 14.7 Hz, 1H), 1.90 (d, J=2.1 Hz, 3H), 1.84 (dd, J=2.1, 13.4 Hz, 1H), 1.60 (m, 2H), 1.34 (s, 3H), 1.07 (s, 9H), 0.74 (m, 2H), 0.59 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.4, 135.5, 133.9, 129.8, 129.5, 129.2, 127.6, 113.8, 88.2, 82.4, 79.1, 77.3, 70.7, 68.2, 67.3, 62.7, 55.2, 48.2, 40.6, 30.6, 26.8, 22.6, 19.1, 15.1, 15.0, 8.66, 3.56; HRMS: Calc'd for $C_{34}H_{37}O_4Si$(M-$C_4H_9^+$): 537.2461. Found: 537.2462.

Minor isomer (3*R**,5*S**)-1-{1-[2-(*tert*-butyldiphenylsilyloxy)-ethyl]-cyclopropyl}-5-(4-methoxyben-zyl-oxy)-3-methyl-octa-1,6-diyn-3-ol (more polar):

IR (film) cm^{-1}: 3503b, 3071m, 3049m, 2931s, 2857s, 2333m, 2066w, 1960w, 1890w, 1774w, 1718w, 1612s, 1588m, 1513s, 1472s, 1428s, 1389s, 1362s, 1302s, 1248s, 1209s, 1173s, 1109s, 1036s, 958s, 911s, 823s, 738s, 703s; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.70 (m, 4H), 7.40 (m, 6H), 7.26 (d, J=8.7 Hz, 2H), 6.86 (d, J=8.7 Hz, 2H), 4.70 (d, J=11.4 Hz, 1H), 4.40 (d, J=11.4 Hz, 1H), 4.32 (m, 1H), 3.87 (t, J=7.2 Hz, 2H), 3.79 (s, 3H), 3.38 (s, 1H), 2.16 (dd, J=7.5, 14.4 Hz, 1H), 1.88 (d, J=2.1 Hz, 3H), 1.67 (m, 1H), 1.59 (t, J=6.9 Hz, 2H), 1.35 (s, 3H), 1.07 (s, 9H), 0.77 (m, 2H), 0.59 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.3, 135.5, 133.9, 129.7, 129.5, 127.9, 127.6, 113.7, 87.8, 83.6, 79.7, 77.9, 69.8, 66.5, 65.9, 62.6, 55.2, 48.2, 40.5, 30.0, 26.8, 19.1, 15.0, 14.9, 8.63, 3.58; HRMS: Calc'd for $C_{34}H_{37}O_4Si$ (M-$C_4H_9^+$): 537.2461. Found: 537.2462.

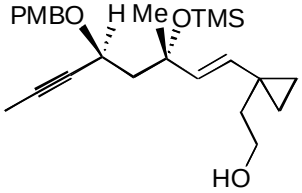


(3*S,5*S**)-1-[1-(2-Hydroxy-ethyl)-cyclopropyl]-5-(4-methxoybenzyloxy)-3-methyl-oct-1-en-6-yn-3-ol**: To (3*S**,5*S**)-1-{1-[2-(*tert*-butyldiphenylsilyloxy)-ethyl]-cyclopropyl}-5-(4-methoxyben-zyl-oxy)-3-methyl-octa-1,6-diyn-3-ol (805 mg, 1.36 mmol) in 5 mL of distilled THF was added Red-Al (1.26 g, 1.22 mL, 4.01 mmol, 65% wt in toluene) at –78°C. The reaction mixture was stirred for 30 min and then warmed to 0°C and stirred at this temperature for 2 h. The solution was then warmed to rt and stirred for 1 h to completion. A very polar spot was identified relative to the starting material. The reaction mixture was cooled to -78°C and quenched with water (0.3 mL). After warming to rt, the reaction mixture was directly filtered through a short silica gel column eluting with diethyl ether. The filtrate was dried with magnesium sulfate followed by concentrating *in vacuo.* The residue was purified by flash chromatography eluting with 5% diethyl ether in petroleum ether to pure diethyl ether afforded (3*S**,5*S**)-1-[1-(2-hydroxy-ethyl)-cyclopropyl]-5-(4-methxoybenzyloxy)-3-methyl-oct-1-en-6-yn-3-ol as a colorless oil (394 mg, 1.10 mmol, 81%).
IR (film) cm^{-1}: 3446b, 3076m, 2923s, 2868s, 2230w, 2060w, 1661w, 1614s, 1586m, 1516s, 1456s, 1424s, 1398s, 1370s, 1330s, 1303s, 1250s, 1174s, 1094s, 1030s, 979s, 822s, 758m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.21 (d, J=8.5 Hz, 2H), 6.84 (d, J=8.5 Hz, 2H), 5.37 (d, J=15.5 Hz, 1H), 5.26 (d, J=15.5 Hz, 1H), 4.65 (d, J=11.5 Hz, 1H), 4.30 (d, J=11.5 Hz, 1H), 4.15 (dd, J=2.0, 9.0 Hz, 1H), 4.01 (s, 1H), 3.76 (d, J=0.5 Hz, 3H), 3.58 (t, J=7.5 Hz, 2H), 3.46 (s, 1H), 2.09 (dd, J=11.0, 15.0 Hz, 2H), 1.84 (s, 3H), 1.75 (dd, J=2.5, 15.0 Hz, 1H), 1.64 (m, 1H), 1.55 (m, 1H), 1.15 (s, 3H), 0.51 (m, 4H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ 159.4, 133.3, 132.4, 129.9, 129.1, 113.8, 82.4, 76.3, 72.4, 70.1, 66.8, 61.0, 55.1, 47.0, 39.1, 29.6, 18.4, 13.7, 13.3, 3.31; HRMS: Calc'd for $C_{22}H_{28}O_3$ (M-H_2O^+): 340.2038. Found: 340.2040.



(3*R, 5*S**)-1-[1-(2-Hydroxy-ethyl)-cyclopropyl]-5-(4-methoxybenzyloxy)-3-methyl-oct-1-en-6-yn-3-ol**: To (3*R**,5*S**)-1-{1-[2-(*tert*-butyldiphenylsilyloxy)-ethyl]-cyclopropyl}-5-(4-methoxyben-zyl-oxy)-3-methyl-octa-1,6-diyn-3-ol (570 mg, 0.96 mmol) in 5 mL of distilled THF was added Red-Al (597 mg, 0.58 mL, 1.92 mmol, 65%wt in toluene) slowly at 0°C. The mixture was stirred for 1.5 h at 0°C and then warmed to rt. At rt the mixture was stirred for 0.5 h. Without workup, the reaction mixture was directly purified by flash chromatography eluting with 5% diethyl ether in petroleum ether to 50% ethyl acetate in petroleum ether to afford (3*R**,5*S**)-1-[1-(2-hydroxy-ethyl)-cyclopropyl]-5-(4-methxoybenzyloxy)-3-methyl-oct-1-en-6-yn-3-ol (289 mg, 0.807 mmol, 84%) as a colorless oil.
IR (film) cm^{-1}: 3440b, 3070m, 2923s, 2863s, 2059w, 1660w, 1613s, 1586m, 1514s, 1470m, 1445m, 1425m, 1372m, 1332m, 1303m, 1249s, 1175s, 1149m, 1067s, 1034s, 975s, 823s; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.27 (dd, J=4.5, 7.0 Hz, 2H), 6.87 (dd, J=4.5, 7.0 Hz, 2H), 5.46 (m, 2H), 4.72 (d, J=11.5 Hz, 1H), 4.41 (d, J=11.5 Hz, 1H), 4.27 (m, 1H), 3.80 (s, 3H), 3.69 (m, 3H),

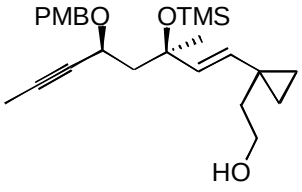
2.02 (dd, J=9.0, 14.0 Hz, 1H), 1.89 (d, J=2.0 Hz, 3H), 1.84 (m, 1H), 1.65 (m, 2H), 1.16 (s, 3H), 0.54 (s, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.2, 133.6, 132.1, 129.9, 129.4, 129.1, 127.3, 113.7, 82.9, 78.5, 71.7, 69.9, 65.9, 61.1, 55.1, 47.1, 39.2, 27.4, 18.6, 13.50, 13.45, 3.48. Anal. Calc'd for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found: C, 73.64; H, 8.50. MS (LRCI) for $C_{22}H_{31}O_4$ $[M+1]^+$: 359.2.



5ii

(3*S,5*S**)-2-{1-[5-(4-Methoxybenzyloxy)-3-methyl-3-trimethylsilyloxy-oct-1-en-6-ynyl] cyclopropyl}-ethanol** (**5ii**): To (3*S**,5*S**)-1-[1-(2-hydroxy-ethyl)-cyclopropyl]-5-(4-methxoybenzyloxy)-3-methyl-oct-1-en-6-yn-3-ol (3.50 g, 9.78 mmol) in 20 mL of distilled dichloromethane was slowly added BSA (1.99 g, 2.41 mL, 9.78 mmol) at rt. The reaction mixture was stirred overnight before another 0.5 eq of BSA (1.00 g, 1.20 mL, 4.89 mmol) was slowly added. The reaction mixture was stirred for another 24 h. The solution was concentrated *in vacuo* and chromatographed eluting with 3% to 30% diethyl ether in petroleum ether to afford **5ii** (3.70 g, 8.60 mmol, 88%) as a pale yellow oil and less than 20 mg of starting material and bis-silyl ether.

IR (film) cm^{-1}: 3508s, 3077w, 2999s, 2956s, 2868s, 2229w, 1659w, 1613s, 1586m, 1514s, 1465m, 1424m, 1397m, 1368m, 1330m, 1302s, 1250s, 1174s, 1091s, 1037s, 978m, 867s, 841s, 757m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.25 (d, J=8.5 Hz, 2H), 6.88 (d, J=8.5 Hz, 2H), 5.36 (d, J=15.5 Hz, 1H), 5.29 (d, J=15.5 Hz, 1H), 4.70 (d, J=11.0 Hz, 1H), 4.34 (d, J=11.0 Hz, 1H), 4.23 (dt, J=2.0, 10.5Hz, 1H), 3.98 (s, 1H), 3.81 (d, J=0.5 Hz, 3H), 3.61 (t, J=8.0 Hz, 2H), 2.14 (dd, J=11.0, 15.0 Hz, 1H), 1.80 (dd, J=2.5, 14.5 Hz, 1H), 1.72 (dt, J=8.0, 14.0 Hz, 1H), 1.60 (dt, J=7.5, 14.0 Hz, 1H), 1.20 (s, 3H), 0.56 (m, 2H), 0.46 (m, 2H), 0.11 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.4, 133.6, 132.1, 129.9, 129.1, 113.8, 82.4, 77.4, 72.5, 70.2, 67.0, 60.8, 55.1, 47.1, 39.2, 29.8, 18.4, 14.2, 13.7, 3.48, -0.55; HRMS: Calc'd for $C_{25}H_{36}O_3Si$ $(M-H_2O^+)$: 412.2434. Found: 412.2437.



5jj

(3*R,5*S**)-2-{1-[5-(4-Methoxybenzyloxy)-3-methyl-3-trimethylsilyloxy-oct-1-en-6-ynyl] cyclopropyl}-ethanol** (**5jj**): To a solution of (3*R**,5*S**)-1-[1-(2-hydroxy-ethyl)-cyclopropyl]-5-(4-methxoybenzyloxy)-3-methyl-oct-1-en-6-yn-3-ol (289 mg, 0.807 mmol) in 2 mL of distilled dichloromethane at rt was added BSA (246 mg, 0.3 mL, 1.21 mmol). The solution was stirred at rt overnight. The resulting mixture was chromatographed eluting with 3% to 70% diethyl ether in petroleum ether without workup to afford bis(trimethylsilyl) ether (32 mg, 0.064 mmol, 8%),

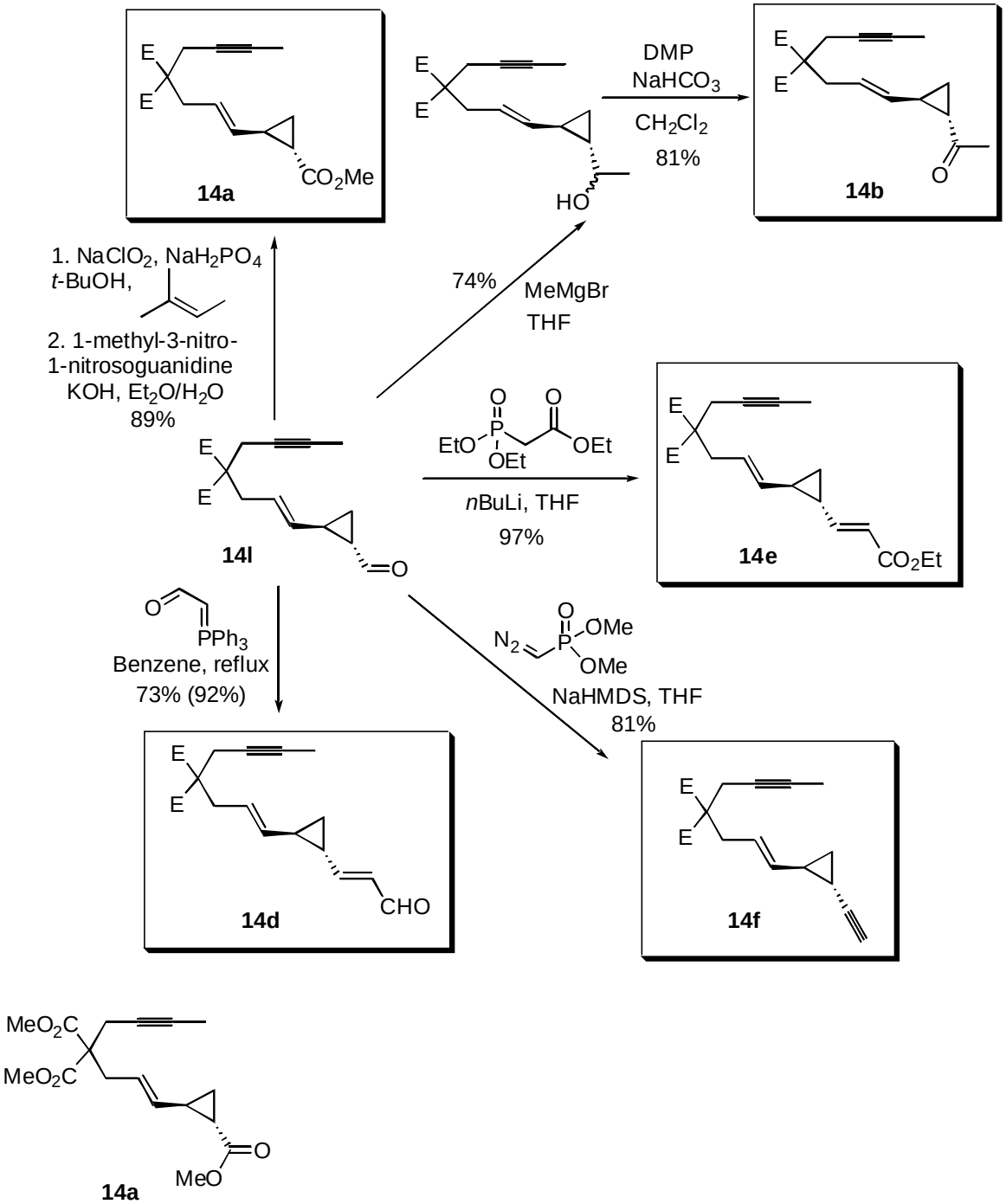
monosilyl ether **5jj** (178 mg, 0.414 mmol, 51%) and recovered starting material (69 mg, 0.19 mmol, 24%).

Or: To (3*R**,5*S**)-1-[1-(2-hydroxy-ethyl)-cyclopropyl]-5-(4-methxoybenzyloxy)-3-methyl-oct-1-en-6-yn-3-ol (320 mg, 0.89 mmol) in 0.5 mL of dichloromethane was added BSA (5 mL) at rt. The mixture was stirred at rt for 4 h. Without workup, the mixture was directly chromatographed (Careful when loading on silica gel the mixture because it is exothermic) eluting with 5% to 20% diethyl ether in petroleum ether to afford alcohol **5jj** (340 mg, 0.79 mmol, 89%) as a colorless oil.

IR (film): 3515b, 3076w, 2957s, 2867m, 1613m, 1586w, 1514s, 1461m, 1391w, 1302m, 1250s, 1176m, 1092s, 1038m, 974m, 842s, 755m cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.15 (d, *J*=8.7 Hz, 2H), 6.74 (d, *J*=8.7 Hz, 2H), 5.26 (s, 2H), 4.60 (d, *J*=11.1 Hz, 1H), 4.28 (d, *J*=11.1 Hz, 1H), 4.16 (m, 1H), 3.67 (s, 3H), 3.52 (t, *J*=7.5 Hz, 2H), 3.12 (bs, 1H), 1.91 (dd, *J*=15.0 Hz, 1H), 1.76 (s, 3H), 1.73 (dd, *J*=4.2, 15.0 Hz, 1H), 1.54 (m, 2H), 1.05 (s, 3H), 0.73 (m, 2H), 0.41 (d, *J*=5.1 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.3, 133.2, 132.4, 129.9, 129.2, 113.7, 82.9, 77.7, 71.7, 70.0, 66.0, 65.8, 55.2, 47.1, 39.3, 27.5, 18.4, 14.1, 11.3, 3.43, -0.59; HRMS: Calc'd for $C_{24}H_{35}O_4Si$(M-Me^+): 415.2305. Found: 415.2304.

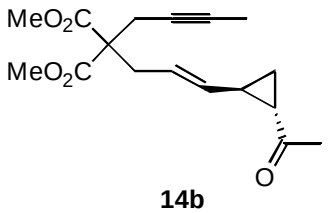
Substrates in Table 3:

14 a, b, d, e, f:



Dimethyl-*trans*-2-but-2-ynyl-2-[3-(2-methoxycarbonyl-cyclopropyl)-allyl]-malonate (**14a**): To a slurry of sodium chlorite (80%, 186 mg, 1.60 mmol), and sodium dihydrophosphate monohydrate (192 mg, 1.60 mmol) in 0.5 mL of distilled water was added a solution of aldehyde **14l** (48 mg, 0.16 mmol) in 1.0 mL of *tert*-butanol and 0.5 mL of 2-methyl-2-butene at rt. Aldehyde **14l** was prepared according to the procedure described in the supplemental material

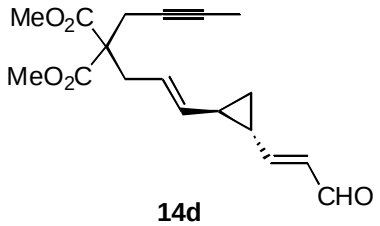
and in the literature.[32] The resulting solution was stirred at rt for 3 h. The mixture was then concentrated *in vacuo*. The residue was diluted with 5 mL of ethyl acetate and washed with 0.001 N HCl (pH = 3). The aqueous layer was extracted with ethyl acetate (2 x 10 mL). The combined organic extracts were washed with brine (3 mL), dried with magnesium sulfate and then concentrated *in vacuo*. The residue was dissolved in about 1 mL of ethyl acetate in a new Erlenmeyer flask without ground joint. In a new test-tube containing 1-methyl-3-nitro-1-nitrosoguanidine (118 mg, 0.80 mmol) was added 2 mL of diethyl ether followed by 0.5 mL of 20% aqueous potassium hydroxide solution at rt. The ether layer was at effervescence and turned bright yellow. After 15 min, the ether layer (not with aqueous layer) was transferred with a pipette to the acid solution generated above. The solution was shaken from time to time at rt. After 1 h, TLC indicated that the reaction was complete. Three drops of glacial acetic acid was added and the solution was stirred for 5 min. The solution was then washed with brine, dried with magnesium sulfate. After the concentration *in vacuo*, ester **14a** (46 mg, 0.14 mmol, 89%) was obtained as a pale yellow oil without further purification.
IR (film) cm^{-1}: 2958s, 2921s, 2850s, 1734s, 1438m, 1383w, 1288m, 1262m, 1200s, 1077m, 1030w, 974w, 802w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.39 (dt, 1 H, *J*=7.5, 15.0 Hz), 5.14 (dd, 1 H, *J*=8.1, 15.3 Hz), 3.70 (s, 6 H), 3.65 (s, 3 H), 2.68 (m, 4 H), 1.94 (m, 1 H), 1.73 (s, 3 H), 1.56 (m, 1 H), 1.32 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 173.8, 170.4, 134.7, 124.2, 78.9, 73.2, 57.3, 52.6, 51.7, 35.2, 29.6, 24.7, 23.0, 21.6, 15.6, 3.42; HRMS: Calc'd for $C_{17}H_{22}O_6$ (M^+): 322.1416. Found: 322.1419.



14b

Dimethyl *trans*-2-[3-(2-acetylcyclopropyl)-allyl]-2-but-2-ynyl-malonate (**14b**): To a solution of alcohol **3.142** (31 mg, 0.10 mmol) in 0.5 mL of dichloromethane was added sodium bicarbonate (12 mg, 0.05 mmol) and DMP (51 mg, 0.12 mmol) at rt. The reaction mixture was stirred at rt for 3 h. Without workup the residue was purified by chromatograph eluting with 5% to 25% diethyl ether in petroleum ether to afford ketone **14b** (25 mg, 0.082 mmol, 81%) as a colorless oil.
IR (film) cm^{-1}: 3003w, 2955m, 2923w, 2854w, 1733s, 1698s, 1438s, 1397m, 1360m, 1326m, 1290s, 1213s, 1056m, 1029w, 967m, 914w, 860w, 749w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.40 (dt, *J*=7.5, 15.0 Hz, 1H), 5.18 (dd, *J*=8.5, 15.0 Hz, 1H), 3.74 (s, 6H), 272 (m, 4H), 2.26 (s, 3H), 1.94 (m, 2H), 1.77 (s, 3H), 1.42 (m, 1H), 0.97 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 207.0, 170.4, 135.0, 124.0, 78.9, 73.2, 57.3, 52.6, 35.1, 30.6, 30.2, 27.5, 23.0, 17.8, 3.48; HRMS (EI+) Calc'd for $C_{17}H_{22}O_5$: 306.1467. Found: 306.1460.

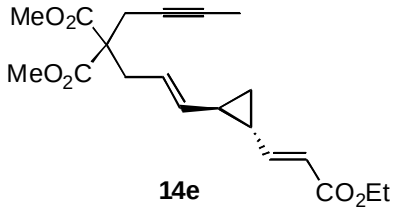
[32] Wender, P. A.; Dyckman, A. J. *Org. Lett.* **1999**, *13*, 2089.



14d

Dimethyl *trans*-2-but-2-ynyl-2-{3-[2-(3-oxo-propenyl)-cyclopropyl]-allyl}-malonate (**14d**): A solution of aldehyde **14l** (38 mg, 0.13 mmol) and formylmethylene triphenylphosphine (40 mg, 0.13 mmol) in 1 mL of distilled benzene was heated at reflux for 10 h. The reaction mixture was filtered and washed with 5 mL of diethyl ether. The organic filtrate was then concentrated *in vacuo* and the resiude was purified by flash chromatography eluting with 5 % to 30 % diethyl ether in petroleum ether to afford *a*, *b*–unsaturated aldehyde **14d** (30 mg, 0.09 mmol, 73%, 92% brsm) and 8 mg recovered starting material **14l**.

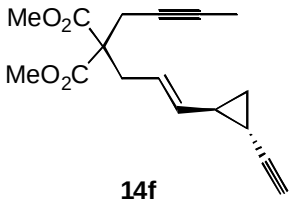
IR (film) cm^{-1}: 2956s, 2923s, 2851m, 1732s, 1682s, 1633m, 1436m, 1290m, 1208m, 1054m, 969m, 927w, 862w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.41 (d, 1H, *J*=7.8Hz), 6.31(dd, 1H, *J*=9.6, 15.3Hz), 6.15 (dd, 1H, *J*=7.8, 15.6Hz), 5.39 (dt, 1H, *J*=7.5, 15.3Hz), 5.20 (dd, 1H, *J*=8.0, 15.3Hz), 3.72 (s, 6H), 2.72 (m, 4H), 1.75 (s, 3H), 1.68 (m, 1H), 1.19 (m, 2 H), 0.86 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 193.1, 170.5, 161.1, 134.9, 130.3, 123.8, 79.0, 73.2, 57.3, 52.7, 35.2, 26.6, 24.7, 23.0, 17.5, 3.5; HRMS: Calc'd for $C_{18}H_{22}O_5$: 318.1467. Found: 318.1463.



14e

Dimethyl *trans*-2-but-2-ynyl-2-{3-[2-(2-ethoxycarbonyl-vinyl)-cyclopropyl]-allyl}-malonate (**14e**): To a solution of distilled ethyl phosphonoacetate (59 mg, 0.26 mmol) in 1 mL of distilled THF was added *n*-butyllithium (1.6 M, 0.16 mL, 0.26 mmol) at 0°C. The resulting pale yellow solution was stirred at 0°C for 15 min before the solution was added to aldehyde **14l** (70 mg, 0.24 mmol) in 1 mL of distilled THF via cannulation. The resulting yellow solution was warmed to rt and stirred for 30 min. After 30 min, the solution was diluted with diethyl ether (10 mL), washed with distilled water (10 mL). The organic fraction was dried with magnesium sulfate and concentrated *in vacuo*. Flash chromatography eluting with 10%-50% diethyl ether in petroleum ether afforded ester **14e** (84mg, 0.23 mmol, 97 %) as a colorless oil.

IR (film) cm^{-1}: 2985m, 2956s, 2922m, 2849w, 1738s, 1714s, 1440m, 1368w, 1270m, 1209m, 1148m, 1052m, 970w, 858w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.42(dd, 1H, *J*=9.9, 15.3Hz), 5.83(d, 1H, *J*=15.9Hz), 5.33(dt, 1H, *J*=7.2, 15.3Hz), 5.15(dd, 1H, *J*=7.8, 15.0Hz), 4.15(q, 2 H, *J*=6.9Hz), 3.70(s, 6H), 2.69(d, 4H, *J*=6.9Hz), 1.74(s, 3H), 1.62(m, 1H), 1.59(m, 1H), 1.26(t, 3H, *J*=7.2 Hz), 1.01(t, 2 H, *J*=7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 165.7, 161.8, 146.7, 130.8, 118.2, 113.8, 74.1, 68.5, 55.3, 52.6, 47.8, 30.5, 20.5, 19.1, 18.2, 11.6, 9.5, -1.3; HRMS: Calc'd for $C_{18}H_{21}O_6$ (M^+-C_2H_5): 333.1338. Found: 333.1346.

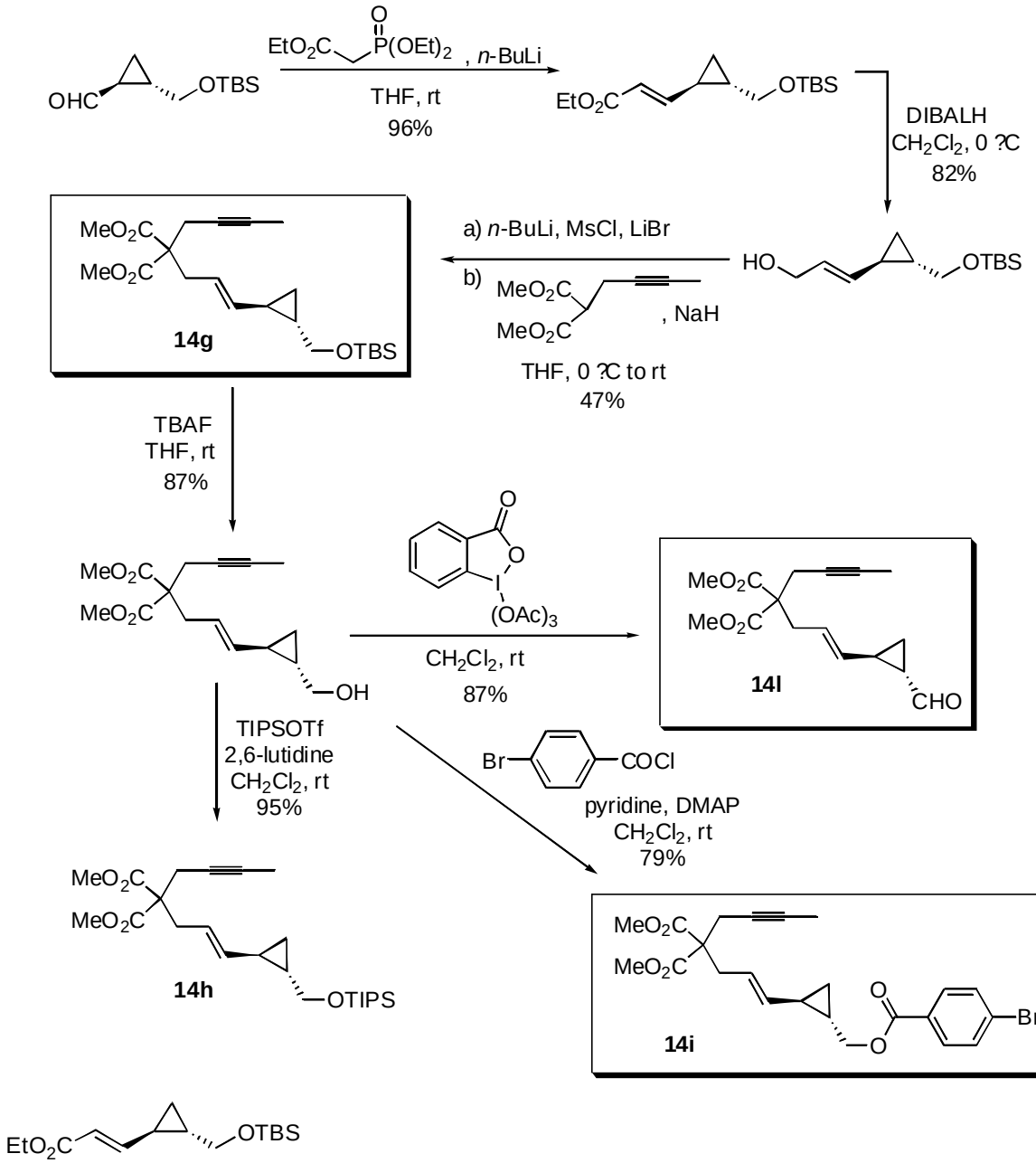


14f

Dimethyl *trans*-2-but-2-ynyl-2-[3-(2-ethynyl-cyclopropyl)-allyl]-malonate (**14f**): To a solution of dimethyl diazomethyl phosphonate (22 mg, 0.15 mmol) in 0.5 mL of distilled THF was slowly added sodium bis(trimethylsilyl)amide (0.15 mL, 0.15 mmol, 1 M in THF) at -78°C. After 5 min a brown solution was formed. To this solution at -78°C was added a solution of malonate aldehyde **14l** (36 mg, 0.12 mmol) in 0.5 mL of distilled THF. Upon the aldehyde addition, the effervescence was observed. After stirring at -78°C for 30 min, the reaction mixture was quenched with water (2 mL). After extraction of the reaction mixture with diethyl ether (2 x 30 mL), the organic fraction was dried over magnesium sulfate and concentrated *in vacuo* to give **14f** (29 mg, 0.10 mmol, 81 %) as a slightly yellow oil.

IR (film) cm^{-1}: 3288m, 3006w, 2955m, 2922m, 2850w, 2112w, 1798s, 1438s, 1289s, 1212s, 1056m, 968w, 860w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.37 (dt, *J*=7.8, 15.0 Hz, 1 H), 5.12 (dd, 15.0 Hz, 1H, *J*=8.4), 3.72 (s, 6 H), 2.71 (s, 2 H), 2.69 (d, *J*=7.8 Hz, 2 H), 1.85 (d, *J*=1.8 Hz, 1 H), 1.75 (s, 3 H), 1.25 (m, 2 H), 1.06 (m, 1 H), 0.85 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.5, 135.3, 123.5, 85.9, 78.9, 73.2, 64.8, 57.3, 52.6, 35.2, 24.4, 23.0, 15.9, 8.43, 3.48; HRMS: Calc'd for $C_{16}H_{17}O_3$ (M^+–CH_3O): 257.1178. Found: 257.1160.

14g, 14h, 14i, 14l:

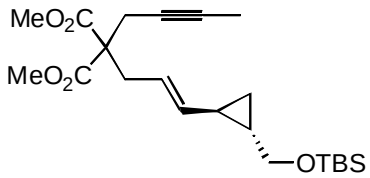


Ethyl-*trans*-3-[2-(*tert*-butyldimethylsilyloxymethyl)-cyclopropyl]-acrylate: To a solution of ethyl phosphonoacetate (421 mg, 0.37 mL, 1.76 mmol) in 2 mL of distilled THF at 0 °C was added *n*-butyllithium (1.10 mL, 1.76 mmol, 1.6 M in hexane). The resulting colorless clear solution was stirred at rt for 10 min. To this solution was added a solution of *trans*-2-*tert*-butyldimethylsilyloxymethyl-cyclopropanecarbxyaldehyde[33] (343 mg, 1.60 mmol) in 2 mL of distilled THF. After 10 min, a white precipitate was formed. After 3 h, the solution was diluted

[33] Wender, P. A.; Dyckman, A. J. *Org. Lett.* **1999**, *13*, 2089.

with 50 mL of diethyl ether before the addition of water (5 mL). The organic layer was dried over magnesium sulfate. Concentration of the filtrate *in vacuo* gave a yellow oil, which was purified using silica gel flash chromatography (5% to 10% diethether in petroleum ether) to afford ethyl-*trans*-3-[2-(*tert*-butyldimethylsilyloxymethyl)-cyclopropyl]-acrylate (438 mg, 1.54 mmol, 96 %) as a yellow oil.
IR (film) cm^{-1}: 2957s, 2930s, 2858s, 1740s, 1472w, 1370m, 1239s, 1094s, 1019m, 838s, 776s; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.48 (dd, *J*=9.9, 15.6 Hz, 1 H), 4.16 (q, *J*=7.2 Hz, 2 H), 3.61 (t, *J*=5.1 Hz, 2 H), 1.27 (t, *J*=7.2 Hz, 3 H), 0.88 (s, 9 H), 1.51 (m, 1 H), 0.84 (m, 3 H), 0.044 (s, 6 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 160.3, 152.7, 118.2, 64.4, 60.0, 25.9, 24.6, 19.4, 14.3, 13.0, -5.22.
HRMS: Calc'd for $C_{15}H_{28}O_3Si$: 284.1808. Found: 284.1805.

3-[2-(*tert*-Butyldimethylsilyloxymethyl)-cyclopropyl]-prop-2-en-1-ol: To a solution of ethyl-*trans*-3-[2-(*tert*-butyldimethylsilyloxymethyl)-cyclopropyl]-acrylate (438 mg, 1.54 mmol) in 5 mL of distilled dichloromethane was added diisobutylaluminum hydride (1 M in hexane, 3.16 mL, 3.16 mmol) at 0°C. The resulting colorless solution was stirred for 3 h and then quenched with a saturated aqueous solution of Rochelle's salt (10 mL). The resulting mixture was stirred for 3 h. The organic fraction was dried over magnesium sulfate and concentrated *in vacuo*. The residue was purified by flash chromatography eluting with 20%-50% diethyl ether in petroleum ether to afford 3-[2-(*tert*-butyldimethylsilyloxymethyl)-cyclopropyl]-prop-2-en-1-ol (306 mg, 1.26 mmol, 82 %) as a colorless oil.
IR (film) cm^{-1}: 3357b, 2930s, 2859s, 1472w, 1255m, 1092s, 1006m, 963w, 836s, 776m. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.62 (dt, 1 H, J=6.3, 15.0 Hz), 5.22 (dd, 1 H, J=8.7, 15.3 Hz), 3.99 (b, 2 H), 3.55 (dd, 1 H, J=6.0, 10.8 Hz), 3.46 (dd, 1 H, J=6.0, 10.8 Hz), 2.34 (b, 1 H), 1.27 (m, 1 H), 1.00 (m, 1 H), 0.84 (s, 9 H), 0.64 (m, 1 H), 0.55 (m, 1 H), 0.00 (s, 6 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 135.4, 126.7, 65.5, 63.2, 25.9, 22.7, 18.7, 18.3, 11.4, -5.3. Anal. Calc'd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 64.59; H, 10.70.

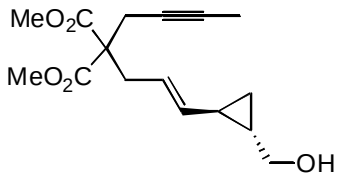


14g

Dimethyl *trans*-2-{3-[2-(*tert*-butyldimethylsilyloxymethyl)-cyclopropyl]-allyl}-2-but-2-ynyl-malonate (**14g**): To a degassed (with argon) solution of malonate ester **A** (130 mg, 0.69 mmol) in 1.5 mL of distilled dichloromethane was added palladium dibenzylideneacetone chloroform complex (36 mg, 0.035 mmol) and triphenylphosphine (55 mg, 0.21 mmol) at rt. To this reaction mixture was then added a solution of allylic carbonate (215 mg, 0.69 mmol) in 1.5 mL of distilled dichloromethane. The color of the solution changed from dark brown to bright organge. To this solution was added triethylamine (77 mg, 0.11 mL, 0.76 mmol). The color of the solution turned red. The solution was stirred at rt for 24 h. After the removal of solvent *in vacuo*, flash chromatography eluting with 5% to 10% diethyl ether in petroleum ether afforded **14g** (208 mg, 0.51 mmol, 74 %) as a colorless oil.

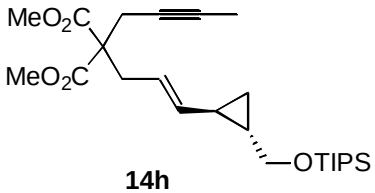
Or: To a solution of allylic alcohol (306 mg, 1.26 mmol) in 3 mL of distilled THF at −78°C was added *n*-butyllithium (0.87 mL, 1.39 mmol, 1.6M in hexane). The resulting solution was stirred for 10 min to afford a slightly yellow solution. To this solution was added distilled methanesulfonyl chloride (0.11 mL, 159 mg, 1.39 mmol) slowly followed by the quick addition of anhydrous lithium bromide (about 121 mg, 1.1 mmol, dried at 100°C in vacuum oven for 3 h). The mixture was stirred at −78°C for 2.5 h to generate bromide *in situ*, which was directly submitted to the next reaction without work-up. To a slurry of sodium hydride (53 mg, 60%, 1.32 mmol, washed with distilled hexane once) in 1 mL of THF at 0°C was added a solution of malonate ester **A** (232 mg, 1.26 mmol) in 3 mL of distilled THF over 15 min to give a slightly cloudy solution. To this solution by canulation was added bromide generated *in situ* by the procedure described above. The resulting white cloudy solution was stirred at rt for 6 h. The solution was diluted with 15 mL of diethyl ether and washed with 10 mL of water. The organic fraction was dried with anhydrous magnesium sulfate. After the removal of solvent *in vacuo*, the residue was purified by flash chromatography eluting with 5%-20% diethyl ether in petroleum ether to afford **14g** (240 mg, 0.59 mmol, 47%, brsm 52%) as a colorless oil, accompanied with the recovery of 3-[2-(*tert*-butyldimethylsilyloxymethyl)-cyclopropyl]-prop-2-en-1-ol (32 mg, 0.13 mmol).

IR (film) cm^{-1}: 3004w, 2958s, 2931s, 2859s, 1740s, 1436mk, 1329w, 1288w, 1262m, 1212m, 1089m, 962w, 836m, 777m; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.28(dt, 1H, *J*=7.2, 15.0Hz), 5.15(dd, 1H, *J*=7.8, 15.0Hz), 3.72(s, 6H), 3.57(dd, 1H, *J*=5.7, 10.8Hz), 3.48(dd, 1H, *J*=6.0, 10.8Hz), 2.71(m, 2 H, *J*=2.4Hz), 2.69(d, 2 H, *J*=7.2 Hz), 1.74(d, 3H, *J*=2.1Hz), 1.25(m, 1H), 1.01(m, 1H), 0.88(s, 9H), 0.62(m, 1H), 0.52(m, 1H), 0.04(s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 165.7, 133.1, 116.0, 73.8, 68.6, 60.8, 52.7, 47.7, 30.4, 21.1, 18.1, 17.9, 14.2, 13.5, 6.5, -1.4, -10.0; HRMS: Calc'd for $C_{22}H_{36}O_5Si$: 408.2332. Found: 408.2330.



Dimethyl *trans*-2-but-2-ynyl-2-[3-(2-hydroxymethyl-cyclopropyl)-allyl]-malonate: To a solution of **14g** (130 mg, 0.32 mmol) in 1.5 mL of distilled THF was added tetrabutylammonium fluoride (0.48 mL, 0.48 mmol, 1 M in THF) at rt. The resulting light brown solution was stirred for 2 h. After the removal of solvent *in vacuo*, the residue was purified by flash chromatography (ether/petroleum ether=10% to 50%) to afford dimethyl *trans*-2-but-2-ynyl-2-[3-(2-hydroxymethyl-cyclopropyl)-allyl]-malonate **(**82 mg, 0.28 mmol, 87 %) as a colorless oil.

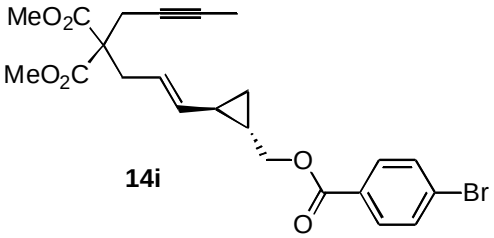
IR (film) cm^{-1}: 3406b, 3002m, 2955m, 2923m, 2850m, 1734s, 1664w, 1438s, 1329m, 1290s, 1211s, 1056m, 1026m, 967m, 868w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.27(m, 1H), 5.18(m, 1H), 3.72(s, 6H), 3.48(m, 2 H), 2.70(m, 4H), 1.74(d, 3H, *J*=1.8Hz), 1.43(s, 1H), 1.28(m, 1H), 1.09(m, 1H), 0.62(m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 165.8, 132.6, 116.5, 74.0, 68.5, 61.4, 52.7, 47.8, 30.4, 18.1, 18.0, 14.6, 6.7, -1.4; HRMS: Calc'd for $C_{14}H_{19}O_3$ (M^+-$C_2H_3O_2$): 235.1334. Found: 235.1354.



14h

Dimethyl-*trans*-2-but-2-ynyl-2-[3-(2-triisopropylsilyloxymethylcyclopropyl)-allyl]-malonate (**14h**): To a solution of dimethyl-*trans*-2-but-2-ynyl-2-[3-(2-hydroxymethylcyclopropyl)-allyl]-malonate (10 mg, 0.034 mmol) in 0.3 mL of dichloromethane were added 2,6-lutidine (11 mg, 0.10 mmol) and TIPSOTf (16 mg, 0.05 mmol). The resulting solution was stirred at rt for 2 h. Without further workup, the mixture was purified by flash chromatography eluting with 1/10 of diethyl ether/petroleum ether to afford silyl ether **14h** (15 mg, 0.032 mmol, 95%) as a colorless oil.

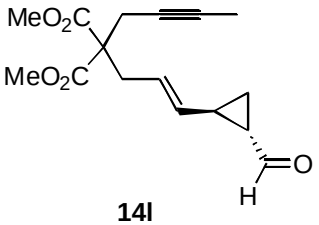
IR (film): 2945, 2866, 1742, 1463, 1437, 1288, 1211, 1093, 1068, 882 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.24 (dt, *J* = 15.2 and 7.2 Hz, 1H), 5.15 (dd, *J* = 15.2 and 8.2 Hz, 1H), 3.69 (s, 6H), 3.63 (dd, *J* = 10.6 and 5.5 Hz, 1H), 3.57 (dd, *J* = 10.6 and 5.7 Hz, 1H), 2.69 (q, *J* = 2.5 Hz, 2H), 2.67 (d, *J* = 7.2 Hz, 2H), 1.73 (t, *J* = 2.5 Hz, 3H), 1.27 (m, 1H), 1.03 (m, 22H), 0.65 (dt, *J* = 8.4 and 5.0 Hz, 1H), 0.49 (dt, *J* = 8.4 and 4.8 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.6, 138.1, 120.6, 78.7, 73.4, 65.3, 57.6, 52.6, 35.3, 22.9, 22.8, 18.7, 18.0, 12.0, 11.3, 3.5; HRMS (EI+) Calc'd for $C_{25}H_{42}O_5Si$: 450.2802. Found: 450.2821.



14i

5,5-Bis(methoxycarbonyl)-8-[*trans*-2-(4-bromobenzoyloxymethyl)cycloprop-1-yl]-oct-7(*E*)-en-2-yne (**14i**): To a solution of dimethyl-*trans*-2-but-2-ynyl-2-[3-(2-hydroxymethylcyclopropyl)-allyl]-malonate (39 mg, 0.132 mmol), 4-*N*,*N*-dimethylaminopyridine (5 mg, 0.041 mmol) and pyridine (15 mL, 0.185) in methylene chloride (1 mL) was added 4-bromobenzoyl chloride (32 mg, 0.145 mmol). After 6 h at room temperature, the reaction mixture was diluted with diethyl ether (10 mL) and washed with 1N sodium bisulfate (3 x 10 mL), dried ($MgSO_4$) and concentrated *in vacuo.* Flash chromatography eluting with 5:1 petroleum ether: diethyl ether afforded **14i** (50 mg, 79%) as a slightly yellow liquid.

IR (film): 3002, 2952, 2855, 2118, 1738, 1591, 1438, 1398, 1270, 1211, 1113, 1102, 1069, 1012, 758 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.92 (d, J = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 1H), 5.35 (dt, *J* = 15.2 and 7.4 Hz, 1H), 5.21 (dd, *J* = 15.2 and 8.2 Hz, 1H), 4.22 (dd, *J* = 11.5 and 7.0 Hz, 1H), 4.17 (dd, *J* = 11.5 and 7.1 Hz, 1H), 3.72 (s, 6H), 2.73 (m, 4H), 1.77 (t, *J* = 2.4 Hz, 3H), 1.43 (m, 1H), 1.27 (m, 1H), .0.79 (dt, *J* = 8.4 and 5.3 Hz, 1H), 0.70 (dt, *J* = 8.4 and 5.1 Hz, 1H) ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.5, 165.9, 136.7, 131.7, 131.1, 129.2, 128.0, 122.0, 78.8, 73.3, 68.4, 57.5, 52.6, 47.2, 35.2, 23.0, 19.9, 19.1, 12.0, 3.5.

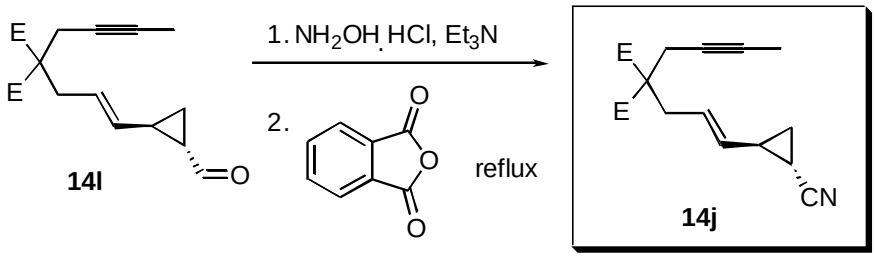


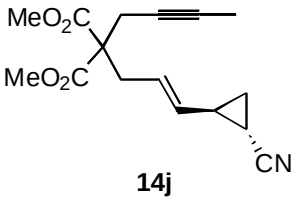
14l

Dimethyl-*trans*-2-but-2-ynyl-2-[3-(2-formylcyclopropyl)-allyl]-malonate (**14l**): To a suspension of sodium bicarbonate (39mg, 0.46mmol) and dimethyl *trans*-2-but-2-ynyl-2-[3-(2-hydroxymethyl-cyclopropyl)-allyl]-malonate (90mg, 0.31mmol) in 0.6mL of distilled dichloromethane was added Dess-Martin periodinane (157mg, 0.37mmol). The resulting white suspension was stirred at rt for 2 h. After 2 h, withour workup, the mixture was purified by flash chromatography eluting with 1:1 petroleum ether and diethyl ether to afford aldehyde **14l** (79mg, 0.27mmol, 87%) as a colorless oil.

IR (film) cm^{-1}: 3007w, 2956m, 2845m, 2737w, 1734s, 1705s, 1438m, 1288m, 1214s, 1056m, 969m, 918w, 861w, 668w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.10 (d, 1H, J=4.9Hz), 5.43 (dt, 1H, J=7.5, 15Hz), 5.16 (dd, 1H, J=8.1, 15.0Hz), 3.70 (s, 3H), 2.70 (d, 2 H, J=7.6Hz), 2.69(s, 2 H), 2.07(m, 1H), 1.83(m, 1H), 1.73(t, 3H, J=2.1Hz), 1.47(m, 1H), 1.13(m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 199.6, 170.4, 133.6, 124.9, 79.0, 73.1, 57.2, 52.6, 35.1, 31.4, 24.7, 23.0, 15.0, 3.4; HRMS: Calc'd for $C_{15}H_{17}O_5$ (M^+-CH_3): 277.1076. Found: 277.1064.

14j:





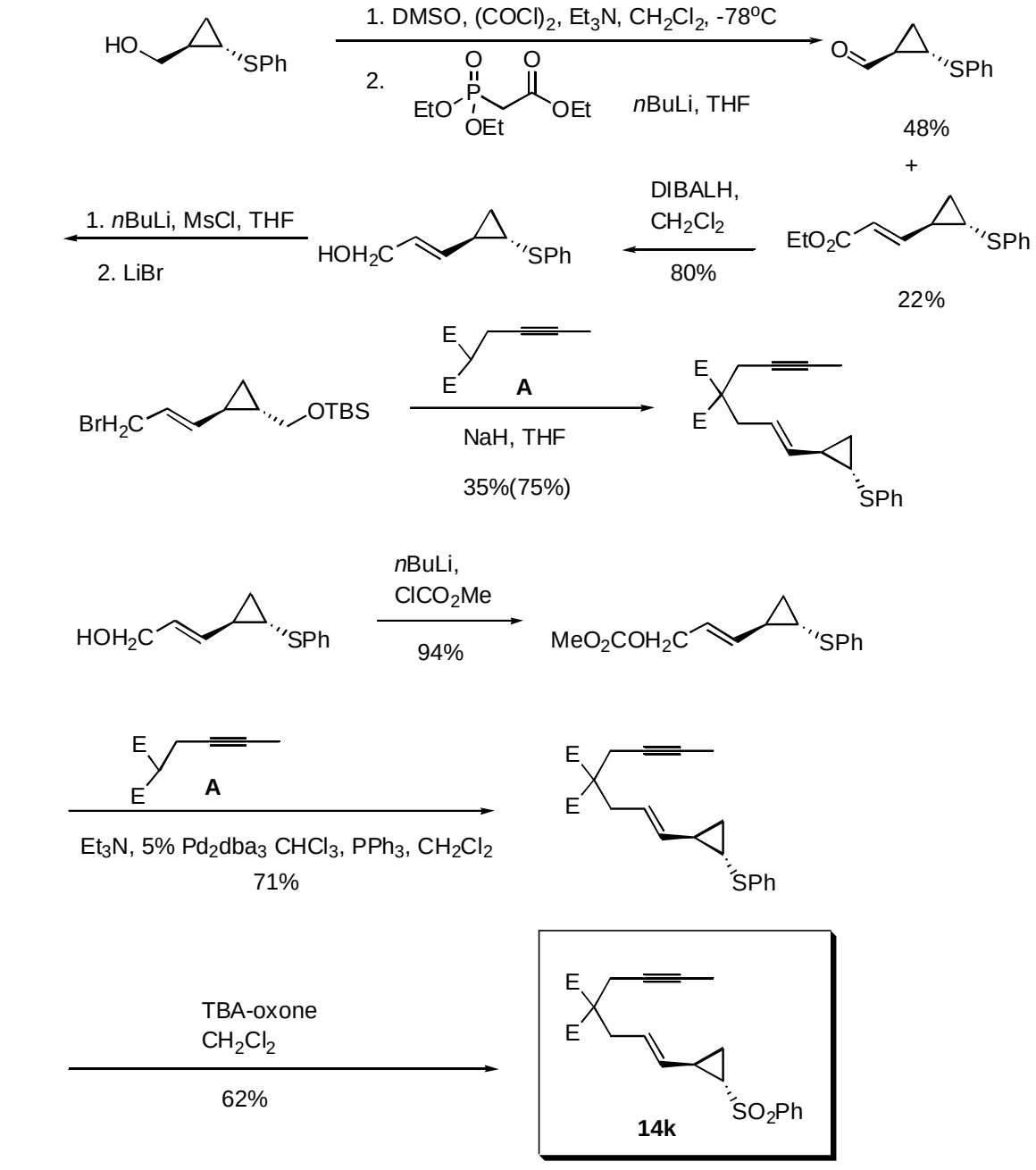
14j

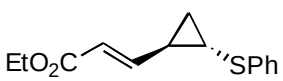
Dimethyl *trans*-2-but-2-ynyl-2-{3-[2-(2-cyano-cyclopropyl]-allyl}-malonate (**14j**)**:** To a cold solution of hydroxylamine hydrochloride (17 mg, 0.25 mmol) and triethylamine (36 ul, 26 mg, 0.26 mmol) in 0.5 mL of distilled acetonitrile was at 0 °C added aldehyde **14l** (65 mg, 0.223 mmol) in 1 mL of distilled acetonitrile. The resulting solution was stirred for 30 min. To this solution was added phthalic anhydride (33 mg, 0.23 mmol). The solution was heated at 80 °C for 8 h. Without workup, the resiude was purified by chromatography eluting with 5%-10% diethyl ether in petroleum ether to afford cyanide **14j** (33 mg, 0.087 mmol, 39 %) as a colorless oil.

IR (film) cm^{-1}: 2955m, 2018s, 2849m, 2237m, 1734s, 1437m, 1288m, 1202s, 1056m, 968w, 862w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.47 (dt, *J*=7.8, 14.7 Hz, 1 H), 5.14 (dd, *J*=7.5, 15.0 Hz, 1 H), 3.73 (s, 6 H), 2.71 (m, 4 H), 2.05 (m, 1 H), 1.76 (t, 2.4 Hz, 3 H), 1.38 (m, 2 H), 1.06 (m, 1

H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.3, 132.3, 126.4, 120.9, 79.1, 73.0, 57.1, 52.7, 35.1, 29.7, 23.2, 14.2, 4.66, 3.48; HRMS: Calc'd for $C_{16}H_{18}O_4N$ ($M\text{-}H^+$): 288.1236. Found: 288.1228.

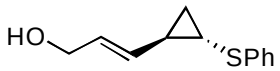
14k:



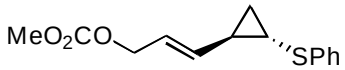


***trans*-3-(2-Phenylsulfanyl-cyclopropyl)-acrylic acid ethyl ester**: To a solution of oxallyl chloride (distilled, 1.05 mL, 12.0 mmol) in 10 mL of distilled methylenechloride at –78°C was slowly added a solution of dimethylsulfoxide (distilled, 1.80 mL, 25.4 mmol) in 5 mL of distilled

methylenechloride. After 30 min, to this mixture was slowly added a solution of 2-phenylsulfanylcyclopropylmethanol[34] (1.80 g, 10.0 mmol) in 5 mL of distilled methylenechloride. After stirring for an additional 90 min, to the mixture was added distilled triethylamine (5.6 mL, 40.2 mmol) at −78 °C and the solution was warmed to 0°C and stirred at 0 °C for 40 min. In another flame-dried flask, to a solution of ethyl phosphonoacetate (1.98 mL, 2.24 g, 10.0 mmol) in 10 mL of distilled THF at 0°C was added *n*-butyllithium (1.6 M in hexane, 6.56 mL, 10.5mmol). This solution was stirred at 0°C for 15 min. The resulting slight yellow solution at 0°C was cannulated to the aldehyde solution generated as described above. The reaction mixture was stirred at 0°C for 1 h, warmed to rt and stirred for 36 h. The reaction solution was then diluted with 50 mL of diethyl ether, washed with 15 mL of 1N HCl, dried with magnesium sulfate and concentrated *in vacuo*. The residue was purified by flash chromatography eluting with 4% diethyl ether in petroleum ether to afford aldehyde (850 mg, 4.78 mmol, 48 %) and *trans*-3-(2-phenylsulfanyl-cyclopropyl)-acrylic acid ethyl ester (550 mg, 2.22 mmol, 22 %) as a colorless oil.
IR (film) cm^{-1}: 3058m, 2982s, 1715s, 1646s, 1584m, 1481m, 1440m, 1378w, 1280m, 1166m, 1145m, 1094w, 1038w, 978w, 916w, 825w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.28(m, 4H), 7.15(m, 1H), 6.56(dd, 1H, *J*=9.9, 15.3Hz), 5.95(d, 1H, *J*=15.6Hz), 4.20(q, 2 H, *J*=6.9 Hz), 2.42(m, 1H), 1.84(m, 1H), 1.36(m, 1H), 1.30(t, 3H, *J*=7.2 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 166.3, 149.2, 137.2, 128.9, 126.7, 125.4, 120.4, 60.2, 26.1, 22.3, 17.5, 14.2. Anal. Calc'd for $C_{14}H_{16}SO_2$: C, 67.71; H, 6.49. Found: C, 67.59; H, 6.35.



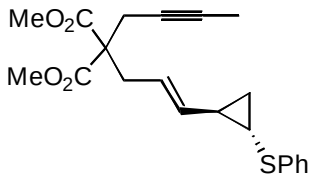
***trans*-3-(2-Phenylsulfanyl-cyclopropyl)-prop-2-en-1-ol**: To a solution of *trans*-3-(2-phenylsulfanyl-cyclopropyl)-acrylic acid ethyl ester (229 mg, 0.92 mmol) in 5 mL of distilled dichloromethane was added diisobutylaluminum hydride(1M in hexane, 2.86 mL, 2.86 mmol) at 0° C. The reaction mixture was stirred at rt overnight to give a colorless solution. The solution was diluted with 20 mL of diethyl ether before the slow addition of 1 N aqueous solution of Rochelle's salt (potassium sodium tartrate, 10 mL). The resulting gel-like mixture was stirred for 30min to afford two layers. The organic layer was washed with brine (5 mL), dried with magnesium sulfate, concentrated *in vacuo*. The residue was purified by flash chromatography eluting with 10% to 50% diethyl ether in petroleum ether to afford *trans*-3-(2-phenylsulfanyl-cyclopropyl)-prop-2-en-1-ol (152 mg, 0.74 mmol, 80 %) as a slightly yellow oil.
IR (film) cm^{-1}: 3355b, 3059m, 3003s, 2922m, 2865s, 1668w, 1584s, 1480s, 1439s, 1244w, 1091s, 1006m, 964s, 841w, 738w, 690s; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.30 (m, 4 H), 7.14 (m, 1 H), 5.80 (dt, 1 H, *J*=5.7, 15.6 Hz), 5.42 (dd, 1 H, *J*=8.7, 15.3 Hz), 4.13 (d, 2 H, *J*=5.4 Hz), 2.19 (m, 1 H), 1.71 (m, 1H), 1.43 (b, 1 H), 1.14 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 138.1, 132.8, 129.1, 128.8, 126.5, 125.1, 63.3, 25.3, 20.1, 16.3; HRMS: Calc'd for $C_{12}H_{14}OS$: 206.0765. Found: 206.0767.



***trans*-3-(2-Phenylsulfanyl-cyclopropyl)-allyl methyl carbonate**: To a solution of *trans*-3-(2-phenylsulfanyl-cyclopropyl)-prop-2-en-1-ol (39 mg, 0.19 mmol) in 0.5 mL of distilled THF was

added *n*-butyllithium (1.6M in hexane, 0.13 mL, 0.21 mmol) at –78°C. The solution turned slightly brown and the reaction mixture was stirred at –78°C for 30 min. To this solution at –78°C was added chloromethylformate (20 mg, 0.016 mL, 0.21 mmol). The mixture was allowed by warm to rt and stirred for 5 h. After 5 h, the solution was washed with water, brine and dried with magnesium sulfate. The solution was then concentrated *in vacuo* to give *trans*-3-(2-phenylsulfanyl-cyclopropyl)-allyl methyl carbonate (47 mg, 94% in two stelps) without further purification.

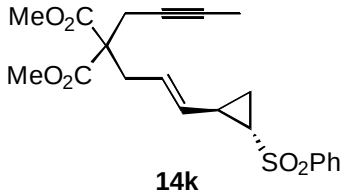
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.29 (m, 4 H), 7.14 (m, 1 H), 5.75 (dt, 1 H, *J*=6.3, 15.6 Hz), 5.51 (d, 1 H, *J*=2.7, 15.3 Hz), 4.60 (d, 2 H, *J*=6.3 Hz), 2.21 (m, 1 H), 1.71 (m, 1 H), 1.19 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 138.0, 136.9, 128.8, 126.5, 125.1, 123.3, 100.2, 68.0, 54.8, 25.4, 20.7, 16.5; HRMS: Calc'd for $C_{14}H_{16}O_3S$: 264.0820. Found: 264.0819.



Dimethyl *trans*-2-but-2-ynyl-2-[3-(2-phenylsulfanylcyclopropyl)-allyl]-malonate: To a solution of *trans*-3-(2-phenylsulfanyl-cyclopropyl)-2-propen-1-ol (89 mg, 0.43 mmol) in 1.5 mL of distilled THF was added *n*-butyllithium (1.6 M in hexane, 0.30 mL, 0.48 mmol) at –78 °C. The resulting solution was stirred for 10 min to afford a slightly yellow solution. To this solution was slowly added distilled methanesulfonyl chloride (0.04 mL, 55 mg, 0.48 mmol) followed by anhydrous lithium bromide (about 40 mg, dried at 100 °C in vacuum oven for 3 h). The mixture was stirred at –78°C for 3 h to generate bromide *in situ*, which was directly submitted to the next reaction without further workup. In another flask containing sodium hydride (19 mg, 60 %, 0.48 mmol) was added a solution of malonate ester **A** (80 mg, 0.43 mmol) in 1.0 mL of distilled THF at rt. The resulting slightly cloudy solution was stirred at rt for 30 min before the mixture was transferred to the bromide solution generated by the procedure described above. The resulting yellow solution was warmed to rt and was stirred for 10 h, diluted with diethyl ether (20 mL), washed with water (5 mL) and brine (5 mL) successively. The organic fraction was dried with magnesium sulfate, concentrated *in vacuo* and separated by flash chromatography eluting with benzene/chloroform/ethanol (95/4/1-90/8/2) to give dimethyl *trans*-2-but-2-ynyl-2-[3-(2-phenylsulfanylcyclopropyl)-allyl]-malonate (56 mg, 0.15 mmol, 35 %) and recovered starting material (47 mg, 0.23 mmol, 75% brsm). (The column was packed with a slurry of silica gel in benzene.)

Or: To a degassed flask (filled with argon) containing palladium dibenzylideneacetone chloroform catalyst (9 mg, 0.0085 mmol), triphenylphosphine (13 mg, 0.051 mmol) and malonate ester **A** (240 mg, 0.69 mmol) was added 0.3 mL of distilled dichloromethane. The resulting orange solution was stirred at rt for 5min. To this solution was added *trans*-3-(2-phenylsulfanyl-cyclopropyl)-allyl methyl carbonate (45 mg, 0.17 mmol) in 0.2 mL of distilled dichloromethane followed by the addition of triethylamine (19 mg, 0.03 mL, 0.19 mmol) to afford a dark brown solution. The solution was stirred at rt for 36 h. After 36h, the solution was concentrated *in vacuo* and the residue was submitted to flash chromatography eluting with 1/4/95 methanol/chloroform/benzene to give dimethyl *trans*-2-but-2-ynyl-2-[3-(2-phenylsulfanylcyclopropyl)-allyl]-malonate as a yellow oil (45mg, 0.12 mmol, 71 %).

IR (film) cm^{-1}: 3002w, 2954m, 2922m, 1734s, 1701w, 1481m, 1437s, 1328w, 1292m, 1211s, 1092m, 1055m, 1026w, 967w, 741m, 691m; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.28 (m, 4 H), 7.13 (m, 1 H), 5.44 (dt, 1 H, *J*=7.5, 15.0 Hz), 5.27 (dd, 1 H, *J*=8.4, 15.3 Hz), 3.73 (s, 6 H), 2.77 (m, 4 H), 2.11 (m, 1 H), 1.76 (s, 3 H), 1.68 (m, 1 H), 1.11 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.5, 138.3, 135.6, 128.8, 126.2, 124.9, 78.9, 73.2, 57.4, 52.6, 35.2, 25.9, 22.9, 20.2, 17.4, 16.0, 3.47; HRMS: Calc'd for $C_{21}H_{24}O_4S$: 372.1395. Found: 372.1388.



14k

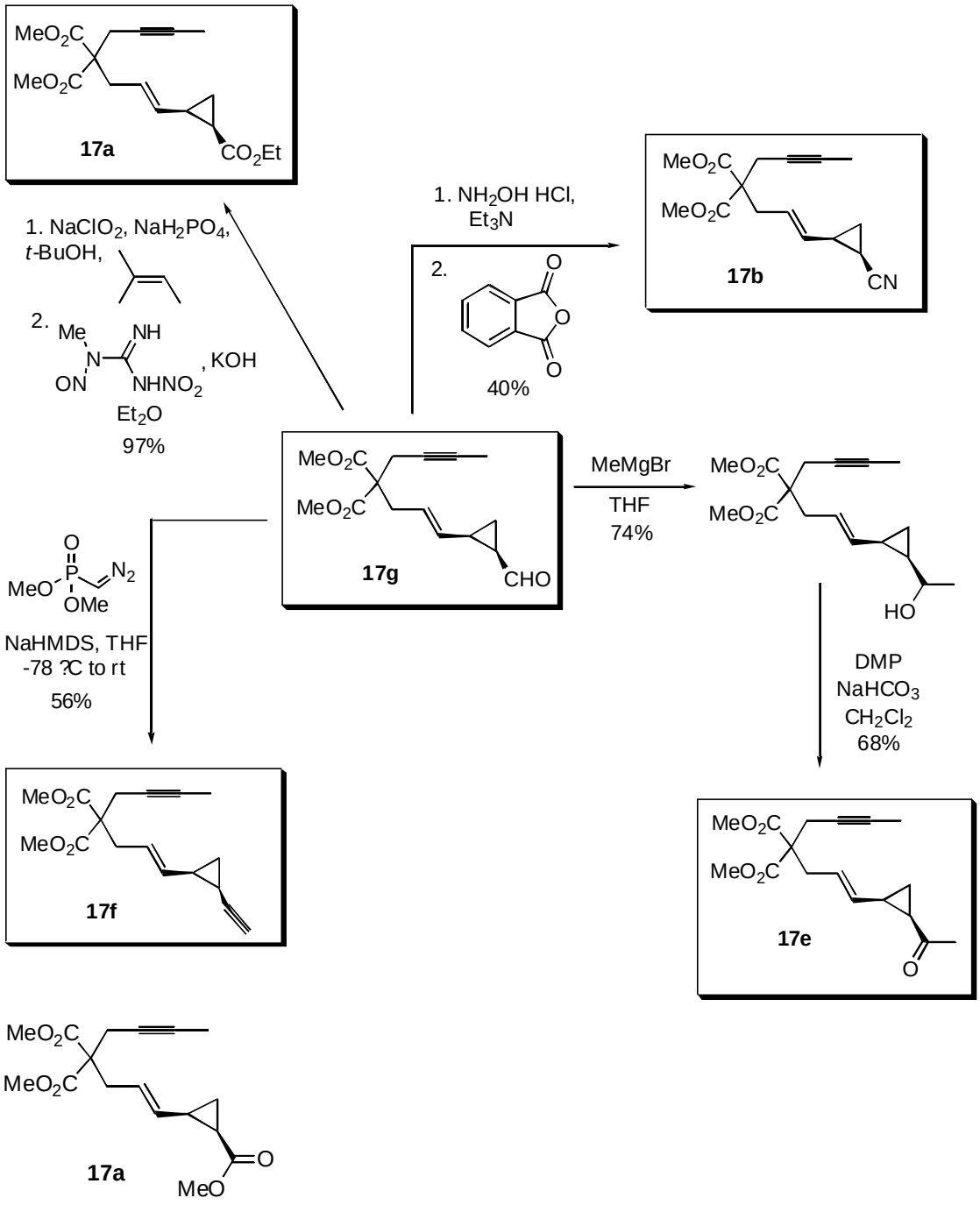
Dimethyl *trans*-2-[3-(2-benzenesulfonylcyclopropyl)-allyl]-2-but-2-ynyl-malonate (**14k**): To a solution of dimethyl *trans*-2-but-2-ynyl-2-[3-(2-phenylsulfanylcyclopropyl)-allyl]-malonate (18 mg, 0.048 mmol) in 0.24 mL of distilled dichloromethane was added tetrabutylammonium oxone[35] (30 %, 201 mg, 0.169 mmol) at rt. The solution was stirred at rt for 3 h. After 3 h, without working up the solution was directly submitted to silica gel chromatography eluting with 30% diethyl ether in petroleum ether to pure diethyl ether to give sulfone **14k** (12 mg, 0.030 mmol, 62%) as a yellow oil.

IR (film) cm^{-1}: 2956s, 2920s, 2847m, 1734s, 1653w, 1437m, 1307m, 1287m, 1212m, 1150s, 1089w, 866w, 734w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.86 (d, 2 H, 6.9 Hz), 7.58 (m, 3 H), 5.43 (dt, 1 H, *J*=7.8, 15.0 Hz), 5.13 (dd, 1 H, *J*=7.2, 15.0 Hz), 3.68 (s, 6 H), 2,65 (d, 2 H, *J*=8.4 Hz), 2.63 (d, 2 H, *J*=2.4 Hz), 2.35 (t, 1 H, *J*=6.9 Hz), 1.71 (t, 3 H, *J*=2.4 Hz), 1.61 (m, 1 H), 1.08 (m, 1 H), 0.86 (m, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.3, 140.6, 133.4, 131.8, 129.3, 127.4, 126.3, 79.1, 73.0, 57.2, 52.7, 40.0, 29.7, 23.1, 22.0, 13.0, 3.47; HRMS: Calc'd for $C_{15}H_{19}O_4$ (M-$C_6H_5SO_2^+$): 263.1278. Found: 263.1283.

[35] Trost, B. M.; Braslau, R. *J. Org. Chem.* **1988**, *53*, 532-537.

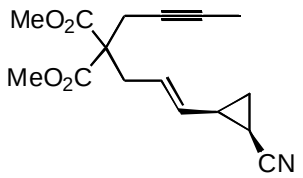
Substrates in Table 4:

17a, 17b, 17e, 17f:



Dimethyl *cis*-2-but-2-ynyl-2-[3-(2-methoxycarbonyl-cyclopropyl)-allyl]-malonate (**17a**): To a solution of sodium chlorite (80%, 46mg, 0.51mmol), sodium dihydrophosphate monohydrate (62mg, 0.51mmol) in 0.2 mL of distilled water was added a solution of aldehyde **17g** (15mg, 0.051mmol) in 0.3 mL of tert-butanol and 0.16 mL of 2-methylbutene at rt. The resulting

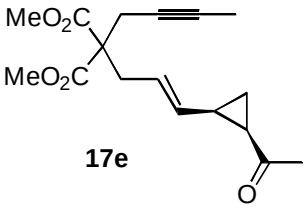
solution was stirred at rt for 6 h. The mixture was then evaporated *in vacuo*. The residue was diluted with ethyl acetate (5 mL) and washed with 0.001N HCl (pH=3). The aqueous layer was extracted with ethyl acetate twice. The combined organic extracts were washed with brine, dried over magnesium sulfate and concentrated *in vacuo*. The residue was dissolved in about 1 mL of ethyl acetate in a new Erlenmeyer flask without a ground joint. In a new test-tube containing 1-methyl-3-nitro-1-nitrosoguanidine (37 mg, 0.25 mmol) at rt was added 1 mL of diethyl ether followed by 0.2 mL of 20% aqueous potassium hydroxide solution. The ether layer was at effervescence and turned bright yellow. After 15 min, the ether layer (be careful not to transfer the aqueous layer) was transferred with a pipette to the acid solution generated before. The solution was shaken from time to time at rt. After 7 h, to the reaction mixture was added one drop of glacial acetic acid. The resulting solution was stirred for 5 min. The solution was then concentrated *in vacuo*. The residue was purified by silica gel flash chromatography eluting with 10% to 60% diethyl ether in petroleum ether to afford ester **17a** (16mg, 0.050mmol, 97%) as a colorless oil.
IR (film) cm^{-1}: 2958m, 2921s, 2850m, 1734s, 1438m, 1383w, 1288m, 1262m, 1200s, 1077m, 1030w, 938w, 802w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.49(m, 2 H), 3.71(s, 6H), 3.67(s, 3H), 2.72(m, 4H), 1.88(m, 1H), 1.75(s, 3H), 1.19(m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 172.3, 170.5, 132.1, 125.3, 78.9, 73.2, 57.5, 52.6, 51.6, 35.3, 23.7, 21.6, 20.7, 14.2, 3.47; HRMS (EI+) Calc'd for $C_{17}H_{22}O_6$: 322.1416. Found: 322.1417.



17b

Dimethyl *cis*-2-but-2-ynyl-2-[3-(2-cyano-cyclopropyl)-allyl]-malonate (**17b**):[36] At 0°C to a solution of hydroxylamine hydrochloride (25 mg, 0.36 mmol) and triethylamine (38 mg, 0.38 mmol, 0.053 mL) in 1 mL of acetonitrle were added aldehyde **17g** (96 mg, 0.33 mmol). The mixture was stirred for 30 min. To this mixture was added phthanic anhydride (54 mg, 0.37 mmol) and the mixture was heated at 80°C for 5 h. Without workup, the mixture was purified by flash chromatography eluting with 10% diethyl ether in petroleum ether to afford cyano product **17b** (38 mg, 0.13 mmol, 40%, a 3:1 mixture of *trans* and *cis* products) as a pale brown oil.
IR (film) cm^{-1}: 3002w, 2956m, 2924m, 2852w, 2237m, 1738s, 1438s, 1329m, 1291s, 1213s, 1162m, 1056m, 1032w, 969m, 859w, 757w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.64 (dt, *J*=8.0, 15.0 Hz, 1H), 5.35 (dd, *J*=7.5, 15.0 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 2.82 (m, 2H), 2.74 (m, 2H), 1.92 (m, 1H), 1.77 (t, *J*=2.5 Hz, 3H), 1.63 (m, 1H), 1.32 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.39, 170.36, 131.1, 127.7, 119.8, 79.2, 73.0, 57.3, 52.82, 52.75, 35.2, 23.1, 20.8, 14.0, 4.49, 3.49. Anal. Calc'd for $C_{16}H_{19}O_4N$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.34; H, 6.69; N, 4.69.

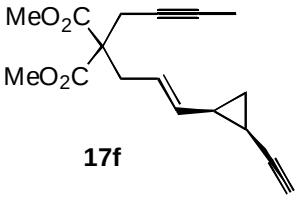
[36] a. Wang, E.-C.; Lin, G.-J. *Tetrahedron Lett.* **1998**, *39*, 4047. b. Alonso, R. A.; Burgey, C. S.; Rao, B. V.; Vite, G. D.; Vollerthun, R.; Zottola, M. A.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1993**, *115*, 6666.



17e

Dimethyl *cis*-2-[3-(2-acetyl-cyclopropyl)-allyl]-2-but-2-ynyl-malonate (**17e**): To a solution of **17g** (40 mg, 0.14 mmol) in 2 mL of THF was added methyl magnesium bromide (0.093 mL, 3 M in Et_2O, 0.28 mmol) at -78°C. This mixture was slowly warmed to rt over 2h. The mixture was purified by flash chromatography eluting with 30% diethyl ether in petroleum ether to afford a mixture of diastereomers of *cis*-2-but-2-ynyl-2-{3-[2-(1-hydroxy-ethylcyclopropyl)-allyl]-dimethyl malonate (31 mg, 0.10 mmol, 74%). To this alcohol (37 mg, 0.12 mmol) in 0.8 mL of dichloromethane were added sodium bicarbonate (15 mg, 0.18 mmol) and DMP (61 mg, 0.14 mmol) at rt. The reaction mixture was stirred at rt for 4 h and without workup directly chromatographed eluting with 15% diethyl ether in petroleum ether to afford ketone **17e** (25 mg, 0.082 mmol, 68%) as a colorless oil.

IR (film) cm^{-1}: 3004w, 2955w, 2923w, 2850w, 1738s, 1698s, 1438m, 1388m, 1291m, 1270m, 1205s, 1165m, 1055m, 975m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.47 (dt, *J*=7.0, 15.5 Hz, 1H), 5.40 (dd, *J*=9.0, 15.0 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 2.72 (m, 4H), 2.25 (m, 1H), 2.24 (s, 3H), 1.99 (t, *J*=8.5 Hz, 1H), 1.78 (s, 3H), 1.37 (m, 1H), 1.15 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 205.7, 170.5, 170.4, 131.8, 125.0, 79.0, 73.1, 57.5, 52.7, 52.6, 35.1, 31.8, 28.9, 26.5, 22.9, 14.8, 3.49; HRMS (EI+) Calc'd for $C_{17}H_{22}O_5$: 306.1467. Found: 306.1473.



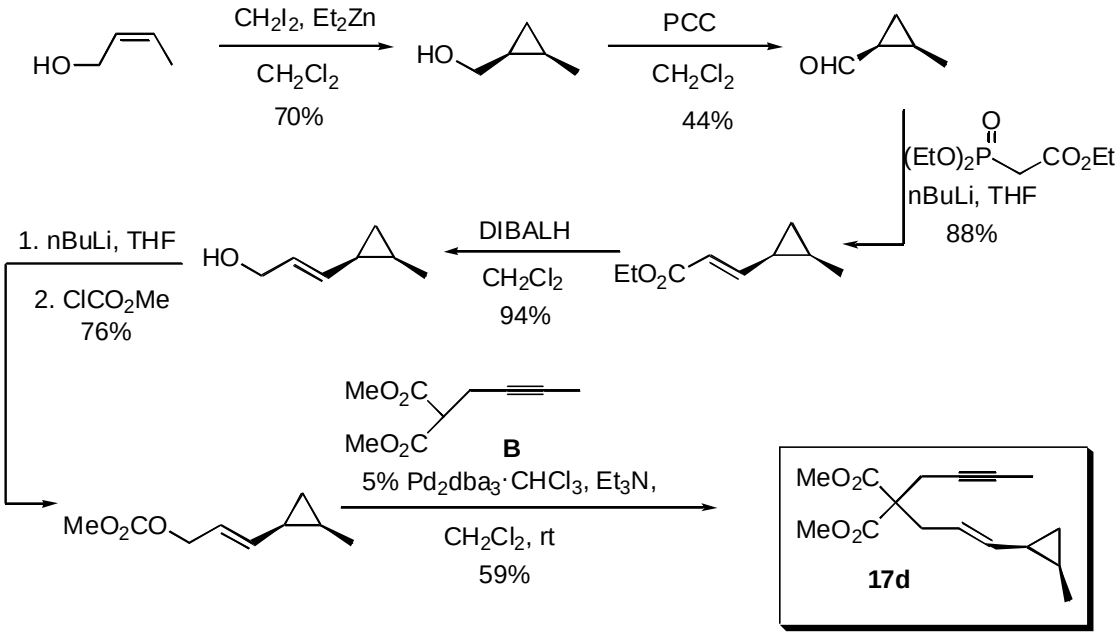
17f

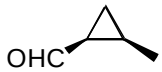
Dimethyl *cis*-2-but-2-ynyl-2-[3-(2-enthynyl-cyclopropyl)-allyl]-malonate (**17f**):[37] To a solution of dimethyl diazomethyl phosphonate (22 mg, 0.15 mmol) in 1 mL of distilled THF at -78°C was added sodium bis(trimethylsilyl)amide (1.0 M, 0.15 mL, 0.15 mmol). After 5 min, to this solution was added a solution of malonate aldehyde **17g** (36 mg, 0.12 mmol) in 0.5 mL of THF. After stirring at -78 °C for 1 h, the solution was warmed to rt for an additional 1 h. Without workup, flash chromatography elutgin with 5% to 20% diethyl ether in petroleum ether afforded **17f** (10 mg, 0.035 mmol, 28%(56% brsm)) as a pale yellow oil.

IR (film) cm^{-1}: 3285m, 3004w, 2955m, 2922m, 2850w, 2116w, 1738s, 1438m, 1325w, 1288m, 1202s, 1053m, 967w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.49 (dt, *J*=7.5, 15.0 Hz, 1H), 5.40 (dd, *J*=8.5, 15.0 Hz, 1H), 3.755 (s, 3H), 3.753 (s, 3H), 2.79 (m, 4H), 1.88 (d, *J*=2.5 Hz, 1H), 1.77 (t, *J*=2.5 Hz, 3H), 1.66 (m, 1H), 1.58 (m, 1H), 1.14 (m, 1H), 0.72 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.58, 170.56, 134.1, 124.4, 84.1, 78.8, 73.3, 66.6, 57.4, 52.7, 52.6, 35.4, 23.0, 20.8, 15.5, 7.3, 3.5; HRMS (EI+) Calc'd for $C_{17}H_{20}O_4$: 288.1362. Found: 288.1359.

17d:

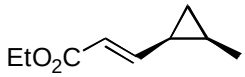
[37] Muller, S.; Liepold, B.; Roth, G. J.; Bestmann, H. T. Synlett, **1996**, 521.





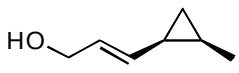
***cis*-2-Methylcyclopropyl-carboxaldehyde**: To a solution of *cis*-2-methylcyclopropyl-1-methanol[38] (800 mg, 9.3 mmol) in 12 mL of dichloromethane was added PCC (4 g, 18.6 mmol) at rt. The mixture was stirred for 3 h and filtered by a silica gel filtration pad and washed with diethyl ether (200 mL). The distillation of solvent afforded *cis*-2-methylcyclopropyl-carboxaldehyde (356 mg, 4.24 mmol, 44%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.38 (m, 1H), 1.85 (m, 1H), 1.51 (m, 3H), 1.11 (d, J=4.5 Hz, 3H).



***cis*-3-(2-Methylcyclopropyl)-ethylacrylate:** To a solution of distilled ethyl phosphonoacetate (378 mg, 1.69 mmol) in 4 mL of distilled THF was added *n*-butyllithium (1.6 M, 1.1 mL, 1.7 mmol) at 0 °C. The resulting pale yellow solution was stirred at 0°C for 15 min. To this solution was added a solution of -2-methylcyclopropyl-carboxaldehyde (89 mg, 1.06 mmol) in 1 mL of distilled THF via cannulation. The resulting yellow solution was stirred at rt for 2 h. The solution was then concentrated *in vacuo* and submitted to silica gel chromatography (eluting with 5%-15% diethyl ether in petroleum ether) to afford *cis*-3-(2-methylcyclopropyl)-ethylacrylate (144 mg, 0.93 mmol, 88%) as a colorless oil.

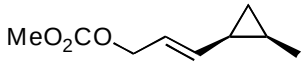
^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.69 (dd, J=5.1, 15.3 Hz, 1H), 5.92 (d, J=15.3 Hz, 1H), 4.18 (q, J=7.2 Hz, 2H), 1.58 (m, 1H), 1.28 (t, J=7.2 Hz, 3H), 1.26 (m, 1H), 1.14 (d, J=6.3 Hz, 3H), 1.10 (m, 1H), 0.47 (q, J=5.1 Hz, 1H).



[38] Hu, S.; Dordick, J. S. *J. Org. Chem.* **2002**, *67*, 314.

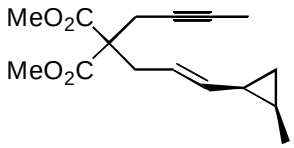
***cis*-3-(2-Methylcyclopropyl)-2-propen-1-ol**: To a solution of *cis*-3-(2-methylcyclopropyl)-ethylacrylate (221 mg, 1.44 mmol) in 4 mL of dichloromethane was added DIBALH (3 mL, 1 M in heptane, 3 mmol) at 0°C. The resulting solution was stirred at rt for 4h. After quenching with the aqueous solution of Rochelle's salt, the aqueous layer was extracted with diethyl ether (3x50 mL). The combined organic layers were dried with magnesium sulfate and concentrated *in vacuo*. The residue was directly purified by flash chromatography eluting with 15% diethyl ether in petroleum ether to afford *cis*-3-(2-methylcyclopropyl)-2-propen-1-ol (152 mg, 1.36 mmol, 94%) as a colorless oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.77 (dt, J=6.3, 15.0 Hz, 1H), 5.43 (dd, J=9.0, 15.3 Hz, 1H), 4.10 (d, J=6.6 Hz, 2H), 1.43 (m, 2H), 1.05 (s, 3H), 0.90 (m, 1H), 0.16 (m, 1H).



***cis*-3-(2-Methylcyclopropyl)-2-propen-1-methyl carbonate**: To a solution of *cis*-3-(2-methylcyclopropyl)-2-propen-1-ol (152 mg, 1.36 mmol) in 2.5 mL of THF was added *n*BuLi (0.94 mL, 1.50 mmol) at -78°C. After 0.5 h, to this mixture was added methyl chloroformate (154 mg, 0.13 mL, 1.63 mmol). The solution was slowly warmed to rt overnight. The mixture was then directly purified by flash chromatography eluting with 5% to 10% diethyl ether in petroleum ether to afford *cis*-3-(2-methylcyclopropyl)-2-propen-1-methyl carbonate (175 mg, 1.03 mmo, 76%) as a pale yellow oil.

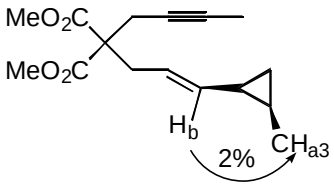
^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.70 (dt, J=6.9, 15.0 Hz, 1H), 5.55 (dd, J=9.0, 15.0 Hz, 1H), 4.58 (d, J=6.9 Hz, 2H), 3.77 (s, 3H), 1.44 (m, 1H), 1.05 (bs, 3H), 1.02 (m, 1H), 0.93 (m, 1H), 0.19 (d, J=4.8 Hz, 1H).



17d

Dimethyl *cis*-2-but-2-ynyl-2-[3-(2-methyl-cyclopropyl)-allyl]-malonate (**17d**): To a degassed flask (filled with argon) containing palladium dibenzylideneacetone chloroform catalyst (20 mg, 0.019 mmol), triphenylphosphine (30 mg, 0.114 mmol) and malonate ester **B** (70 mg, 0.38 mmol) was added 0.8 mL of distilled dichloromethane. The resulting orange solution was stirred at rt for 5 min. To this solution was added carbonate *cis*-3-(2-methylcyclopropyl)-2-propen-1-methyl carbonate (65 mg, 0.38 mmol) in 0.2 mL of distilled dichloromethane followed by the addition of triethylamine (42 mg, 58 uL, 0.42 mmol) to afford a dark brown solution. The solution was stirred at rt for 8 h. After 8 h, without workup, the solution was submitted to flash chromatography eluting with 5% diethyl ether in petroleum ether to give **17d** as a yellow oil (62 mg, 0.22 mmol, 59 %).

IR (film) cm^{-1}: 2999m, 2955s, 2924m, 1739s, 1662w, 1436s, 1392w, 1329m, 1290s, 1208s, 1071m, 1033m, 870m, 905w, 856w, 820w, 743w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.34 (m, 2H), 3.744 (s, 3H), 3.740 (s, 3H), 2.76 (m, 4H), 1.77 (t, *J*=2.5 Hz, 3H), 1.40 (m, 1H), 1.03 (d, *J*=6.0 Hz, 3H), 0.95 (m, 1H), 0.85 (m, 1H), 0.12 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.66, 170.63, 135.2, 122.8, 78.7, 73.4, 57.5, 52.6, 35.5, 22.9, 18.7, 13.8, 12.4, 3.46. Anal. Calc'd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.22; H, 7.78.

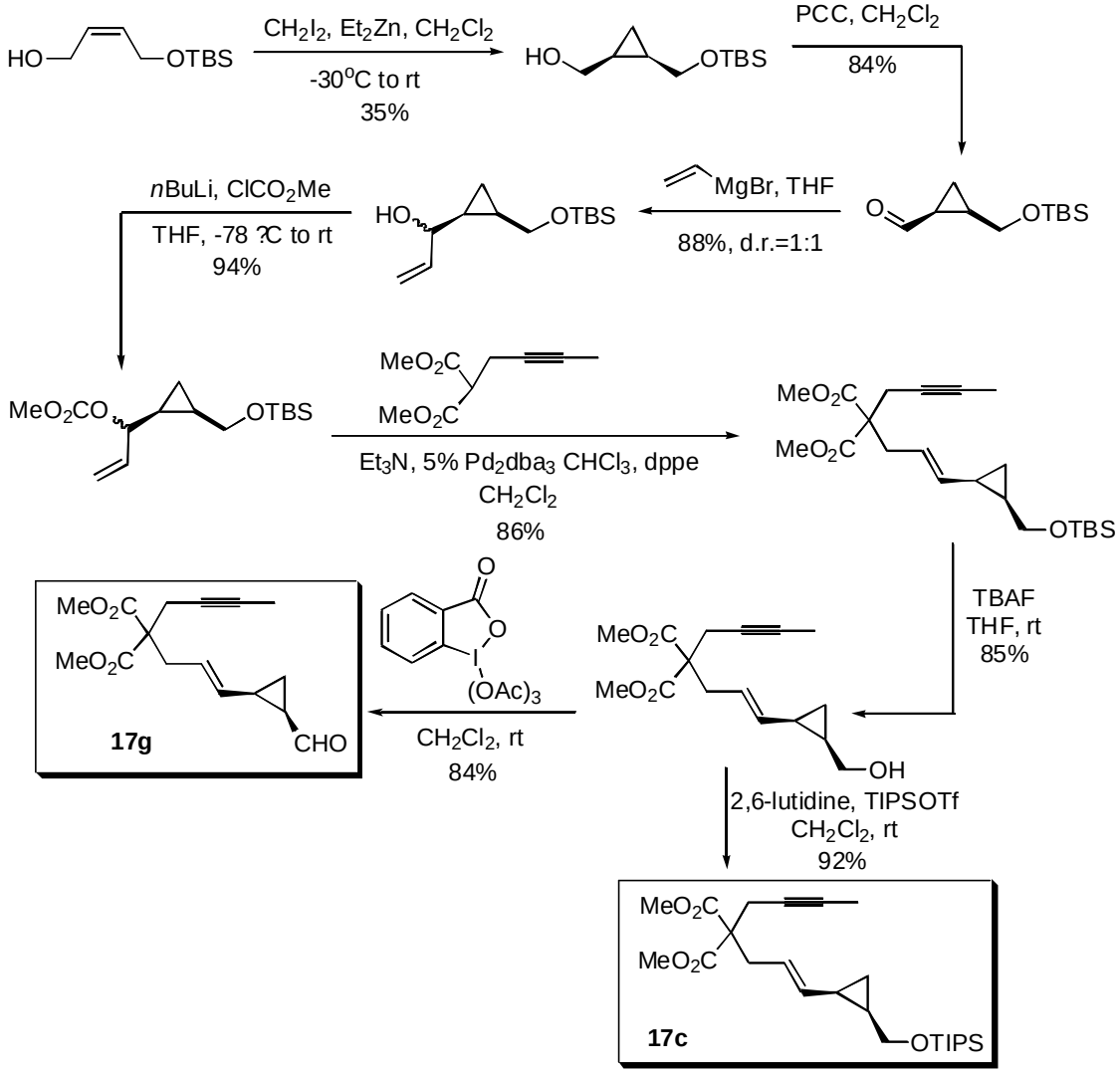


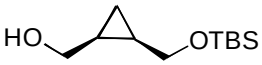
17d

δ_a = 1.03 ppm

δ_b= 5.34 ppm

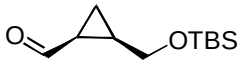
17c, 17g:



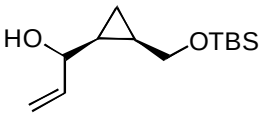


***cis*-[2-(*tert*-Butyldimethylsilyloxymethyl)cyclopropyl]-methanol**: To a rapidly stirred solution of 4-(*tert*-butyl-dimethyl-silanyloxy)-but-2-en-1-ol (2.0 g, 9.88 mmol) in methylene chloride (100 mL), at - 30 ºC, was added diiodomethane (8 mL, 99.3 mmol) followed by careful addition

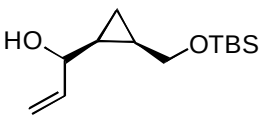
of 1.1M diethylzinc (45 mL, 49.5 mmol). The resulting turbid white suspension is slowly warmed to room temperature, stirred for 12 h and then poured into 1N hydrochloric acid (100 mL). The resulting biphasic solution was extracted with diethyl ether (3 x 50 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 6:1 petroleum ether: diethyl ether afforded first the methyl ether of the product (1.05 g, 46%) followed by *cis*-[2-(*tert*-butyldimethylsilyloxymethyl)cyclopropyl]-methanol (750 mg, 35%) as a colorless liquid.
IR (film): 3484, 3002, 2956, 2938, 2858, 1472, 1255, 1057, 935, 777 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.18 (dd, *J* = 11.5 and 5.3 Hz, 1H), 4.00 (dd, *J* = 12.1 and 5.1 Hz, 1H), 3.30 (br s, 1H), 3.28 (q, *J* = 11.5 Hz, 2H), 0.95 (s, 9H), 0.89 (m, 2H), 0.79 (m, 1H), 0.22 (m, 1H), 0.15 (s, 3H), 0.12 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 63.9, 63.2, 25.9, 18.2(2), 17.4, 8.4, -5.3, -5.5.



***cis*-2-(*tert*-Butyldimethylsilyloxymethyl)cyclopropanal**: To a stirred solution of *cis*-[2-(*tert*-butyldimethylsilyloxymethyl)cyclopropyl]-methanol (1.40 g, 6.48 mmol) in methylene chloride (50 mL) was added PCC (2.0 g, 9.28 mmol). After stirring at room temperature for 2 h, the solution was diluted with diethyl ether (100 mL) and filtered through a pad of silica, which was washed with diethyl ether (3 x 50 mL). The filtrate was concentrated *in vacuo* and chromatographed eluting with 6:1 petroleum ether: diethyl ether to afford *cis*-2-(*tert*-Butyldimethylsilyloxymethyl)cyclopropanal (1.17 g, 84%) as a colorless liquid.
IR (film): 2956, 2930, 2858, 1710, 1472, 1255, 1087, 837, 777 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.44 (d, *J* = 5.1 Hz, 1H), 4.00 (dd, *J* = 11.1 and 5.4 Hz, 1H), 3.65 (dd, *J* = 11.1 and 7.7 Hz, 1H), 1.98 (tt, *J* = 8.1 and 5.4 Hz, 1H), 1.80 (m, 1H), 1.36 (dt, *J* = 6.9 and 5.1 Hz, 1H), 1.24 (td, *J* = 8.1 and 4.9 Hz, 1H), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 200.9, 61.0, 27.4, 26.2, 25.8, 18.2, 12.0, -5.3, -5.4.

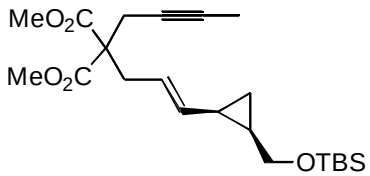


***cis*-1-[2-(*tert*-Butyldimethylsilyloxymethyl)cyclopropyl]-prop-2-en-1-ol**: To a solution of *cis*-2-(*tert*-butyldimethylsilyloxymethyl)cyclopropanal (300 mg, 1.14 mmol) in THF (10 mL) at -78 °C was added 0.9M vinylmagnesium bromide (1.75 mL, 1.58 mmol). The reaction mixture was slowly warmed to room temperature over 1 h and then diluted with diethyl ether (25 mL). The solution was washed with 1N sodium bisulfate (2 x 25 mL), brine (25 mL), dried ($MgSO_4$) and concentrated. Flash chromatography eluting with 2:1 petroleum ether:diethyl ether afforded *cis*-1-[2-(*tert*-butyldimethylsilyloxymethyl) cyclopropyl]-prop-2-en-1-ol (241 mg, 88%) as a colorless liquid
IR (film): 3434, 3002, 2956, 2938, 2858, 1472, 1255, 925, 777 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.02 (m, 1H), 5.33 (d, *J* = 17.3 Hz, 1H), 5.12 (d, *J* = 10.5 Hz, 1H), 4.20 (dd, *J* = 11.6 and 5.2 Hz, 1H), 3.97 (s, 1H), 3.75 (dd, *J* = 9.5 and 5.5 Hz, 1H), 3.31 (t, *J* = 11.3 Hz, 1H), 1.30-1.15 (m, 2H), 0.92 (s, 9H), 0.89 (m, 1H), 0.28 (m, 1H), 0.12 (s, 3H), 0.10 (s, 3H).



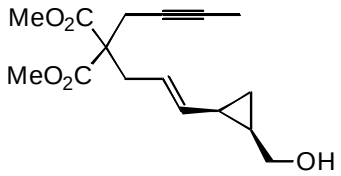
Methyl-*trans*-1-[2-(*tert*-butyldimethylsilyloxymethyl)cyclopropyl]-prop-2-enylcarbonate: To a solution of *cis*-1-[2-(*tert*-butyldimethylsilyloxymethyl) cyclopropyl]-prop-2-en-1-ol (65 mg, 0.270 mmol) in THF (5 mL) at -78 ºC was slowly added 1.5 M butyllithium (0.19 mL, 0.285 mmol). After 15 min., methyl chloroformate (0.48 mL, 0.62 mmol) was slowly added over an additional 15 min. After stirring at -78 ºC for 30 min. the reaction mixture was allowed to warm to room temperature over 30 min. and the turbid white solution quenched by the addition of water (10 mL) and diethyl ether (25 mL). The biphasic mixture was separated and the organic phase washed with 1N sodium bicarbonate (25 mL), brine (25 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 5% diethyl ether: pentanes afforded methyl-*trans*-1-[2-(*tert*-butyldimethylsilyloxymethyl)cyclopropyl]-prop-2-enylcarbonate (76 mg, 94%) as a colorless liquid.

IR (film): 3030, 3002, 2956, 2938, 2858, 1747, 1472, 1255, 925, 778 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.03 (m, 1H), 5.33 (d, *J* = 17.4 Hz, 1H), 5.18 (d, *J* = 10.8 Hz, 1H), 4.88 (dd, *J* = 10.0 and 5.1 Hz, 1H), 3.83 (dd, *J* = 11.2 and 5.6 Hz, 1H), 3.78 (s, 3H), 3.60 (dd, *J* = 11.0 and 7.5 Hz, 1H), 1.30-1.10 (m, 2H), 0.89 (s, 9H), 0.82 (m, 1H), 0.50 (m, 1H), 0.06 (s, 3H), 0.05 (s, 3H).

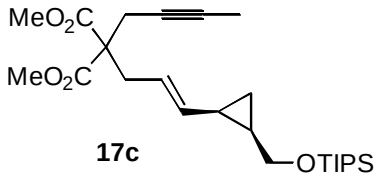


5,5-Bis(methoxycarbonyl)-8-[*trans*-2-(*tert*-butyldimethylsilyloxymethyl)cycloprop-1-yl]-oct-7(*E*)-en-2-yne: To a solution of alkyne **B** (35 mg, 0.190 mmol), Pd_2dba_3•$CHCl_3$ (4 mg, 0.0039 mmol) and diphenylphosphinoethane (5 mg, 0.013 mmol) in methylene chloride (1 mL) was added triethylamine (0.040 mL, 0.287 mmol). After stirring at room temperature for 10 min., a solution of methyl-*trans*-1-[2-(*tert*-butyldimethylsilyloxymethyl)cyclopropyl]-prop-2-enylcarbonate (50 mg, 0.167 mmol) in methylene chloride (1 mL) was added. After an additional 12h, the solution was concentrated *in vacuo* and chromatographed eluting with 6:1 petroleum ether:diethyl ether to afford 5,5-bis(methoxycarbonyl)-8-[*trans*-2-(*tert*-butyldimethylsilyloxymethyl) cycloprop-1-yl]-oct-7(*E*)-en-2-yne (58 mg, 86%) as a colorless liquid.

IR (film): 2954, 2929, 2857, 1741, 1437, 1251, 1207, 1083, 836, 776 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.40 (dd, *J* = 15.1 and 7.5 Hz, 1H), 5.34 (dt, *J* = 15.1 and 7.8 Hz, 1H), 3.75 (s, 6H), 3.61 (dd, *J* = 6.8 and 2.7 Hz, 2H), 2.75 (q, *J* = 2.5 Hz, 2H), 1.78 (t, *J* = 2.5 Hz, 3H), 1.55 (m, 1H), 1.30-1.22 (m, 1H), 0.92 (s, 9H), 0.90 (m, 1H), 0.37 (dd, *J* = 10.7 and 5.5 Hz, 1H), 0.08 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.6, 134.3, 123.4, 78.7, 76.7, 73.4, 63.2, 57.4, 52.6(2), 35.3, 26.0, 20.5, 18.5, 18.4, 10.7, 3.5, -5.2, -5.1.

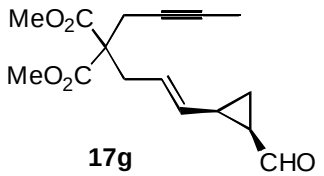


5,5-Bis(methoxycarbonyl)-8-[*cis*-2-(hydroxymethyl)cycloprop-1-yl]-oct-7(*E*)-en-2-yne: To a solution of 5,5-bis(methoxycarbonyl)-8-[*trans*-2-(*tert*-butyldimethylsilyloxymethyl) cycloprop-1-yl]-oct-7(*E*)-en-2-yne (18 mg, 0.044 mmol) in THF (0.4 mL) was added 1.0M tetrabutylammonium fluoride (9 µL, 0.09 mmol) and acetic acid (6 µL, 0.10 mmol). After 6 h at room temperature, the reaction mixture was diluted with diethyl ether (5 mL) and washed with water (3 x 5 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 2:1 petroleum ether: diethyl ether afforded 5,5-bis(methoxycarbonyl)-8-[*cis*-2-(hydroxymethyl)cycloprop-1-yl]-oct-7(*E*)-en-2-yne (11 mg, 85%) as a colorless liquid.
IR (film): 3406, 3002, 2954, 2869, 1738, 1437, 1293, 1207 1150, 1040 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.47 (dd, *J* = 15.0 and 7.4 Hz, 1H), 5.38 (dt, *J* = 15.0 and 7.8 Hz, 1H), 3.75 (s, 6H), 3.38 (t, *J* = 10.3 Hz, 2H), 2.82-2.68 (m, 4H), 1.78 (t, *J* = 2.5 Hz, 3H), 1.70 (br s, 1H), 1.58 (m, 1H), 1.40-1.28 (m, 1H), 0.92 (dt, *J* = 13.1 and 5.2 Hz, 1H), 0.40 (dd, *J* = 10.3 and 5.4 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.6, 133.6, 124.4, 78.9, 73.2, 63.1, 57.5, 52.6, 35.4, 23.0, 20.9, 18.1, 10.7, 3.4.



17c

5,5-Bis(methoxycarbonyl)-8-[*cis*-2-(tri-*iso*-propylsilyloxymethyl)cycloprop-1-yl]-oct-7(*E*)-en-2-yne (**17c**): To a solution of 5,5-bis(methoxycarbonyl)-8-[*cis*-2-(hydroxymethyl)cycloprop-1-yl]-oct-7(*E*)-en-2-yne (25 mg, 0.084 mmol) in methylene chloride (0.8 mL) was added 2,6-lutidine (30 µL, 0.258 mmol) and tri-*iso*-propylsilyl triflate (35 µL, 0.130 mmol). After stirring at room temperature for 2 h, the solution was diluted with diethyl ether (10 mL), washed with 1N sodium bisulfate (2 x 10 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography eluting with 10:1 petroleum ether: diethyl ether afforded **17c** (35 mg, 92%) as a colorless liquid.
IR (film): 2946, 2867, 1741, 1463 1437, 1290, 1207, 1090, 1067, 883, 682 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.42 (dd, *J* = 15.2 and 8.1 Hz, 1H), 5.33 (dt, *J* = 15.2 and 7.3 Hz, 1H), 3.74 (s, 6H), 3.68 (d, *J* = 6.8 Hz, 2H), 2.74 (q, *J* = 2.6 Hz, 2H), 1.76 (t, *J* = 2.6 Hz, 3H), 1.53 (m, 1H), 1.25 (m, 1H), 1.09 (m, 21H), 0.88 (td, *J* = 8.2 and 4.8 Hz, 1H), 0.40 (q, *J* = 5.3 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.6, 134.5, 123.3, 78.7, 73.4, 63.3, 57.4, 52.6, 35.3, 22.8, 20.7, 18.0, 12.3, 12.0, 10.6, 3.5; HRMS (EI+) Calc'd for $C_{25}H_{43}O_5Si$ (M + H^+): 451.2880. Found: 451.2844.

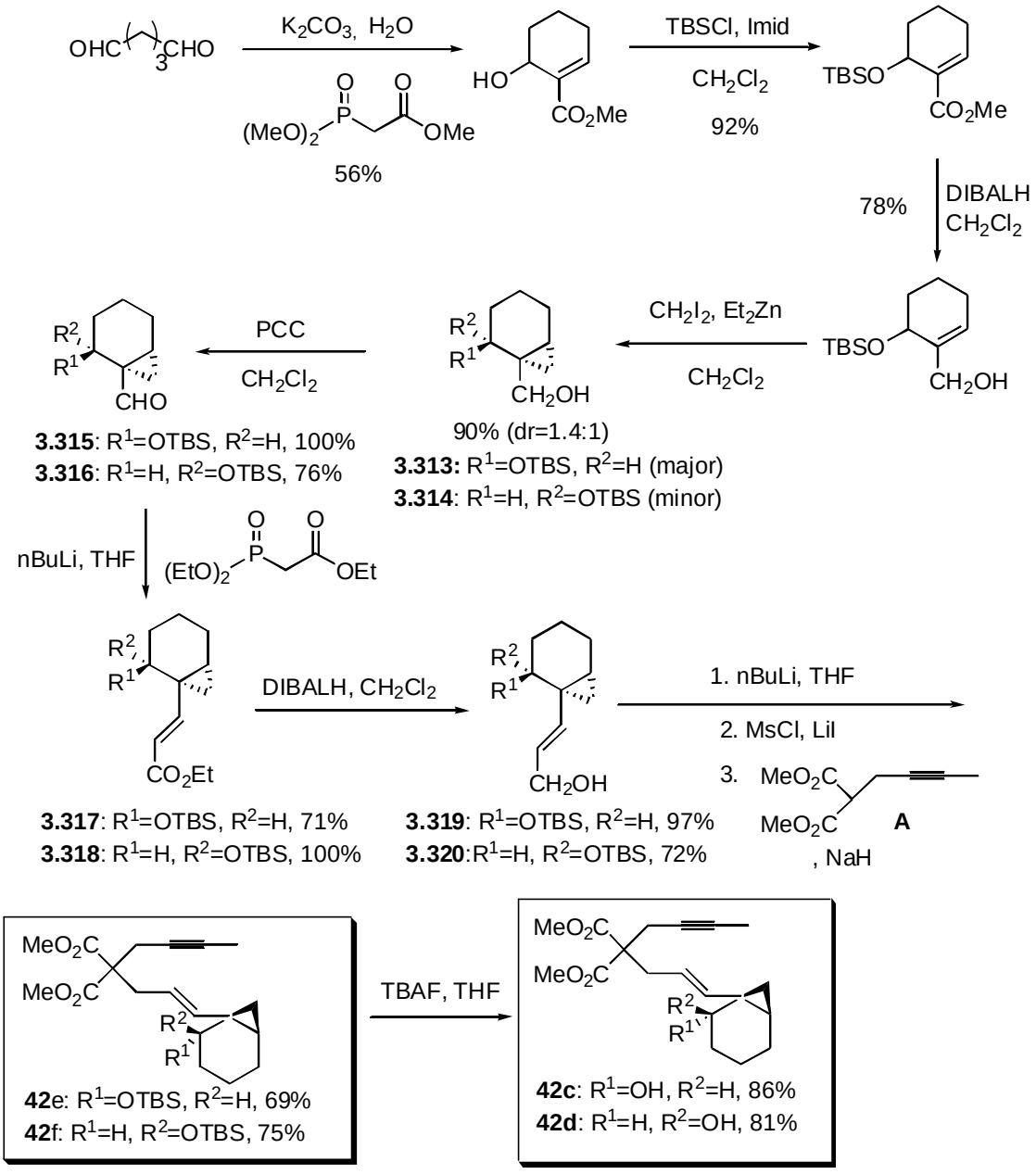


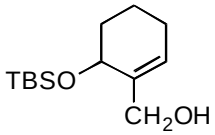
17g

5,5-Bis(methoxycarbonyl)-8-[*cis*-2-formylcycloprop-1-yl]-oct-7(*E*)-en-2-yne (**17g**): To a suspension of sodium bicarbonate (11 mg, 0.13 mmol) and 5,5-bis(methoxycarbonyl)-8-[*cis*-2-(hydroxymethyl)cycloprop-1-yl]-oct-7(*E*)-en-2-yne (25 mg, 0.085 mmol) in methylene chloride (0.8 mL) was added Dess-Martin periodinane (43 mg, 0.10 mmol). After stirring at room

temperature for 2 h, the white suspension was directly chromatographed eluting with 1:1 petroleum ether: diethyl ether to afford **17g** (21 mg, 84 %) as a colorless liquid.
IR (film): 3003, 2954, 2923, 2845, 1736, 1704, 1437, 1291, 1207, 1056, 972 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.28 (d, *J* = 5.1 Hz, 1H), 5.51 (m, 2H), 3.73 (s, 3H), 3.71 (s, 3H), 2.71 (m, 2H), 2.68 (q, *J* = 2.5 Hz, 2H), 2.09 (m, 1H), 1.73 (t, *J* = 2.5 Hz, 3H), 1.44 (dt, *J* = 6.9 and 5.4 Hz, 1H), 1.35 (td, *J* = 8.1 and 5.2 Hz, 1H) ^{13}C-NMR (125 MHz, $CDCl_3$): δ 200.7, 170.4, 131.0, 126.5, 79.0, 73.1, 57.3, 52.7, 35.2, 29.8, 25.9, 23.1, 14.5, 5.5.

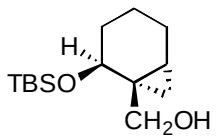
Substrates in Table 5:
42c, d, e, f:

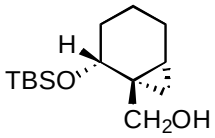




[**6-(*tert*-Butyldimethylsilyloxy)-cyclohex-1-enyl]-methanol**: To a solution of methyl [6-(*tert*-butyldimethylsilyloxy)-cyclohex-1-enyl]-carboxylate[39] (1.09 g, 4.04 mmol) in 8 mL of distilled dichloromethane was added DIBALH (8.5 mL, 1M in heptane) at 0°C. The solution was warmed up to rt and stirred overnight. After quenching the reaction mixture slowly with saturated aqueous solution of Rochelle's salt, the aqueous layer was washed with diethyl ether three times (3 x 60 mL). The organic extracts were combined and concentrated *in vacuo.* The residue was purified eluting with 10% to 60% diethyl ether in petroleum ether to afford [6-(*tert*-butyldimethylsilyloxy)-cyclohex-1-enyl]-methanol as a pale yellow oil (0.759 g, 3.14 mmol, 78%).

IR (film) cm^{-1}: 3362b, 2931s, 2858s, 1670w, 1472m, 1463m, 1438w, 1406w, 1389w, 1361m, 1338w, 1254s, 1164m, 1086s, 1066s, 1021s, 965m, 922m, 899s, 836s, 810m, 775s, 676m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.80 (t, *J*=3.5 Hz, 1H), 4.37 (t, *J*=5.0 Hz, 1H), 4.14 (d, *J*=12.0 Hz, 1H), 4.03 (d, *J*=12.0 Hz, 1H), 2.21 (b, 1H), 2.11 (m, 1H), 2.98 (m, 1H), 1.82 (m, 1H), 1.77 (m , 1H), 1.69 (m, 1H), 1.56 (m, 1H), 0.877 (s, 3H), 0.876 (s, 3H), 0.106 (s, 3H), 0.105 (s, 3H), 0.104 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 139.1, 127.6, 68.8, 65.9, 32.7, 25.8, 25.1, 25.1, 19.3, -4.17, -4.91; HRMS (EI+) Calc'd for $C_{19}H_{26}O_5$: 334.1780. Found: 334.1782.



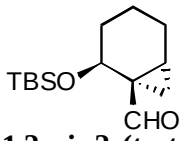


[1,2-*cis*-2-(*tert*-Butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-methanol and **[1,2-*trans*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-methanol**: To a solution of [6-(*tert*-butyldimethylsilyloxy)-cyclohex-1-enyl]-methanol (0.76 g, 3.14 mmol) in 6 mL of distilled dichloromethane was added diiodomethane (2.52 g, 0.76 mL, 9.42 mmol) at 0 °C followed by the slow addition of diethyl zinc (1 M in hexane, 4.7 mL, 4.7 mmol). The reaction mixture was slowly warmed to rt and stirred overnight. The reaction solution was then quenched with saturated sodium bisulfate solution, extracted with diethyl ether (3 x 100 mL). The combined ether extracts were concentrated *in vacuo* and purified by flash chromatography eluting with 5% to 7.5% diethyl ether in petroleum ether to afford two separable diastereomers [1,2-*cis*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-methanol (429 mg, 1.68 mmol, 53%) and [1,2-*trans*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-methanol (300 mg, 1.17 mmol, 37%) as pale yellow oils.

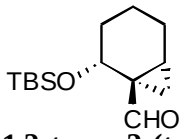
For major isomer [1,2-*cis*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-methanol: IR (film) cm^{-1}: 3388b, 2934s, 2858s, 1463m, 1361w, 1253m, 1084s, 1044m, 1021s, 940w, 875m, 835s, 774s, 668m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.31 (dd, *J*=5.5, 8.5 Hz, 1H), 3.48 (d, *J*=11.0 Hz, 1H), 3.42 (d, *J*=11.0 Hz, 1H), 1.98 (bs, 1H), 1.87 (m, 1H), 1.58 (m, 1H), 1.45 (m, 2H), 1.43

[39] Villieras, M.; Rambaud, S.; Graff, M. *Synth. Commun.* **1986**, *16*, 149.

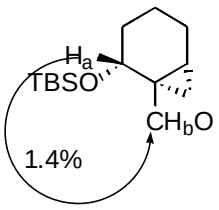
(m, 2H), 1.09 (m, 1H), 0.91 (s, 9H), 0.61 (dd, *J*=5.0, 5.5 Hz, 1H), 0.55 (dd, *J*=5.0, 9.0 Hz, 1H), 0.14 (s, 3H), 0.10 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 71.4, 70.7, 31.0, 28.8, 25.8, 25.6, 23.1, 20.2, 18.8, 18.0, 13.0, -3.81, -4.59. For [1,2-*trans*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-methanol: IR (film) cm^{-1}: 3388b, 2934s, 2858s, 1463m, 1361w, 1253m, 1084s, 1044m, 1021s, 940w, 875m, 835s, 774s, 668m; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 4.18 (dd, *J*=4.2, 4.6 Hz, 1H), 3.96 (d, *J*=10.8 Hz, 1H), 3.01 (b, 1H), 2.82 (d, *J*=11.2 Hz, 1H), 1.93 (m, 1H), 1.61 (m, 2H), 1.35 (m, 2H), 1.26 (m, 3H), 0.91 (s, 6H), 0.90 (s, 3H), 0.43 (ddd, *J*=1.6, 4.8, 9.4 Hz, 1H), 0.13 (s, 3H), 0.08 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 71.7, 70.5, 31.0, 26.4, 25.7, 22.8, 17.9, 17.0, 16.0, 14.9, -4.61, -5.08; HRMS (EI+) Calc'd for $C_{14}H_{28}O_2Si$: 256.1859. Found: 256.1860.



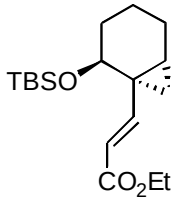
1,2-*cis*-2-(*tert*-Butyldimethylsilyloxy)-bicyclo[4.1.0]heptane-1-carboxylaldehde: To a solution of alcohol [1,2-*cis*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-methanol (54 mg, 0.21 mmol) in 1 mL of distilled dichloromethane was added PCC (68 mg, 0.32 mmol) at 0°C. The reaction mixture was slowly warmed to rt and stirred for 2.5 h. Without workup the solution was submitted to flash chromatography eluting with 5% to 15% diethyl ether in petroleum ether to afford 1,2-*cis*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]heptane-1-carboxylaldehde (52 mg, 0.21 mmol, 100%) as a pale brown oil.
IR (film) cm^{-1}: 2937s, 2858s, 1709s, 1472w, 1252m, 1087s, 1053m, 1026m, 873w, 836s, 777m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.70 (s, 1H), 4.93 (m, 1H), 1.81 (m, 3H), 1.38 (m, 6H), 0.85 (s, 9H), 0.08 (s, 3H), 0.02 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 201.3, 61.5, 38.6, 31.7, 25.7, 23.1, 22.8, 17.9, 15.5, 14.9, -4.74; HRMS (EI+) Calc'd for $C_{14}H_{26}O_2Si$: 254.1702. Found: 254.1700.



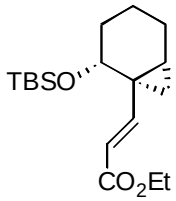
1,2-*trans*-2-(*tert*-Butyldimethylsilyloxy)-bicyclo[4.1.0]heptane-1-carboxylaldehde:
To a solution of [1,2-*trans*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-methanol (207 mg, 0.81 mmol) in 1 mL of distilled dichloromethane was added PCC (349 mg, 1.62 mmol) at 0°C. The reaction mixture was slowly warmed to rt and stirred for 2.5 h. Without workup, the solution was submitted to flash chromatography eluting with 5% to 15% diethyl ether in petroleum ether to afford 1,2-*trans*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]heptane-1-carboxylaldehde (157 mg, 0.62 mmol, 76%) as a colorless oil.
IR (film) cm^{-1}: 2951s, 2859s, 1708s, 1472m, 1464m, 1390w, 1361w, 1256m, 1121s, 1075s, 1026s, 1006m, 911m, 867m, 837s, 809m, 775 s; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.99 (s, 1H), 4.43 (dd, *J*=6.0, 9.5 Hz, 1H), 1.98 (m, 1H), 1.65 (m, 1H), 1.58 (m, 2H), 1.45 (m, 2H), 1.25 (dd, *J*=4.0, 9.5 Hz, 1H), 1.14 (m, 1H), 0.88 (s, 9H), 0.61 (dd, *J*=4.0, 6.5 Hz, 1H), 0.10 (s, 3H), 0.08 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 203.8, 67.0, 35.0, 29.9, 25.8, 14.0, 22.2, 21.8, 18.0, 15.2, -4.44, -4.98, -4.99; HRMS (EI+) Calc'd for $C_{14}H_{26}O_2Si$: 254.1702. Found: 254.1705.
nOe study:



δ_a = 4.43 ppm
δ_b = 9.99 ppm

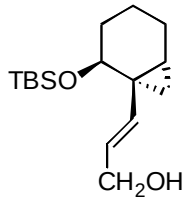


3-[1,2-*cis*-2-(*tert*-Butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-acrylic acid ethyl ester: To a solution of triethyl phosphonoacetate (60 mg, 53 uL, 0.25 mmol) in 1 mL of distilled THF was added *n*-butyllithium (1.6 M in hexane, 0.16 mL, 0.25 mmol) at 0°C. After this solution was stirred at 0°C for 30 min, to this flask was added 1,2-*cis*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]heptane-1-carboxylaldehde (52 mg, 0.21 mmol) in 1 mL of distilled THF. The reaction mixture was slowly warmed to rt and stirred for an additional 2 h. The reaction mixture was concentrated *in vacuo* and separated using flash chromatography eluting with 10% diethyl ether in petroleum ether to afford 3-[1,2-*cis*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-acrylic acid ethyl ester (48 mg, 0.15 mmol, 71%) as a colorless oil.
IR (film) cm^{-1}: 2936s, 2858m, 1719s, 1642m, 1471w, 1463w, 1390w, 1366w, 1308m, 1258m, 1172s, 1088s, 1068m, 1045m, 835s, 774s; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.87 (d, *J*=16.0 Hz, 1H), 5.68 (d, *J*=16.0 Hz, 1H), 4.36 (dd, *J*=5.0, 6.5 Hz, 1H), 4.18 (q, *J*=7.0 Hz, 2H), 1.87 (m, 1H), 1.60 (m, 1H), 1.50 (m, 1H), 1.43 (m, 1H), 1.30 (m, 4H), 1.22 (m, 2H), 1.33 (dd, *J*=5.0, 7.0 Hz, 1H), 0.89 (s, 9H), 0.88 (m, 1H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 167.2, 157.3, 115.3, 68.6, 60.0, 31.4, 29.0, 26.3, 25.8, 23.3, 18.4, 18.2, 18.0, 14.3, -4.08, -4.40; HRMS (EI+) Calc'd for $C_{18}H_{32}O_3Si$: 324.2121. Found: 324.2119.

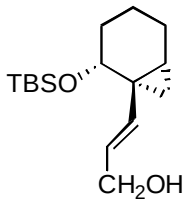


3-[1,2-*trans*-2-(*tert*-Butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-acrylic acid ethyl ester: To a solution of triethyl phosphonoacetate (177 mg, 157 uL, 0.74 mmol) in 1 mL of distilled THF was added *n*-butyllithium (1.6 M in hexane, 0.47 mL, 0.75 mmol) at 0°C. After this solution was stirred at 0°C for 30 min, to this flask was added a solution of 1,2-*trans*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]heptane-1-carboxylaldehde (157 mg, 0.62 mmol) in 1 mL of distilled THF. The mixture was slowly warmed to rt and stirred for additional 2 h. The reaction mixture was concentrated *in vacuo* and separated using flash chromatography eluting with 10% diethyl ether in petroleum ether to afford 3-[1,2-*trans*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-acrylic acid ethyl ester (241 mg, 0.74 mmol, 100%) as a colorless oil.

IR (film) cm^{-1}: 2937s, 2899wm, 2859s, 1716s, 1645m, 1472m, 1464m, 1366m, 1307m, 1259s, 1207w, 1166s,, 1077s, 1045m, 1020m, 990w, 876w, 837s, 775m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J*=16.0 Hz, 1H), 5.44 (dd, *J*=4.5, 16.0 Hz, 1H), 4.12 (q, *J*=7.0 Hz, 2H), 4.11 (m, 1H), 2.02 (m, 1H), 1.62 (m, 2H), 1.44 (m, 2H), 1.26 (t, *J*=7.0 Hz, 3H), 1.25 (m, 1H), 1.17 (m, 1H), 0.93 (m, 1H), 0.92 (s, 9H), 0.59 (dd, *J*=5.0, 6.5 Hz, 1H), 0.12 (s, 3H), 0.06 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 167.0, 154.7, 115.1, 68.7, 59.8, 30.7, 29.6, 26.9, 25.7, 24.4, 22.6, 18.1, 15.2, 14.2, -4.53, -5.00; HRMS (EI+) Calc'd for $C_{18}H_{32}O_3Si$: 324.2121. Found: 324.2121.

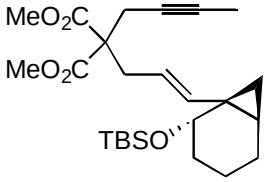


3-[1,2-*cis*-2-(*tert*-Butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-prop-2-en-1-ol: To a solution of ester 3-[1,2-*cis*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-acrylic acid ethyl ester (173 mg, 0.53 mmol) in 2 mL of distilled methylenechloride was added DIBALH (1 M in heptane, 1.11 mL) at 0°C. The solution was stirred for 3 h at rt. After quenching the reaction mixture slowly with saturated Rochelle's salt aqueous solution (5 mL), the aqueous layer was washed with diethyl ether three times (3 x 60 mL). The organic extracts were combined and concentrated *in vacuo* and purified eluting with 10% to 40% diethyl ether in petroleum ether to afford 3-[1,2-*cis*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-prop-2-en-1-ol (144 mg, 0.51 mmol, 96%) as a pale yellow oil.
IR (film) cm^{-1}: 3344b, 3003w, 2935s, 2858s, 1664w, 1472m, 1464m, 1389w, 1361m, 1253s, 1185w, 1086s, 1042s, 1019s, 955m, 883m, 836s, 813m, 775s, 669m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.67 (d, *J*=15.0 Hz, 1H), 5.50 (dt, *J*=6.5, 15.5 Hz, 1H), 4.19 (dd, *J*=5.5, 7.5 Hz, 1H), 4.07 (dd, *J*=0.5, 6.5 Hz, 1H), 1.84 (m, 2H), 1.49 (m, 2H), 1.39 (m, 2H), 1.26 (m, 1H), 1.15 (m, 2H), 0.86 (s, 9H), 0.82 (m, 1H), 0.68 (dd, *J*=5.0, 9.0 Hz, 1H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 140.4, 124.5, 70.1, 63.9, 31.4, 27.8, 25.83, 25.77, 23.4, 23.3, 19.2, 16.4, -4.08, -4.27; HRMS (EI+) Calc'd for $C_{16}H_{30}O_2Si$: 282.2015. Found: 282.2016.



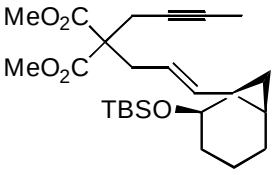
3-[1,2-*trans*-2-(*tert*-Butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-prop-2-en-1-ol: To a solution of 3-[1,2-*trans*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-acrylic acid ethyl ester (241 mg, 0.74 mmol) in 3 mL of distilled methylenechloride was added DIBALH (1 M in heptane, 1.15 mL) at 0°C. The solution was stirred for 3 h at rt. After quenching the reaction mixture slowly with saturated Rochelle's salt aqueous solution, the aqueous layer was washed with diethyl ether three times (3 x 60 mL). The organic layer was combined and concentrated *in vacuo*. The residue was purified eluting with 10% to 40% diethyl ether in petroleum ether to afford 3-[1,2-*trans*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-prop-2-en-1-ol as a pale yellow oil (150 mg, 0.53 mmol, 72%).

IR (film) cm^{-1}: 3347b, 3066w, 3004w, 2936s, 2858s, 1664w, 1172m, 1163m, 1406w, 1389w, 1361m, 1349w, 1255s, 1171w, 1116s, 1076s, 1019s, 966m, 938w, 913w, 836s, 809m, 774s, 729w, 671w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.21 (d, *J*=15.6 Hz, 1H), 5.37 (dt, *J*=6.3, 15.6 Hz, 1H), 4.06 (m, 3H), 1.99 (m, 1H), 1.55 (m, 2H), 1.38 (m, 3H), 1.12 (m, 1H), 0.89 (s, 9H), 0.76 (dd, *J*=4.5, 9.3 Hz, 1H), 0.33 (t, *J*=5.1 Hz, 1H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 138.0, 124.6, 69.3, 64.0, 29.6, 26.4, 25.9, 22.7, 20.8, 18.2, 15.3, -4.54, -4.74; HRMS (EI+) Calc'd for $C_{16}H_{30}O_2Si$: 282.2015. Found: 282.2012.



42e

Dimethyl 2-{3-[*cis*-1,2-(bicyclo[4.1.0]-2-*tert*-butyldimethylsilyloxy-hept-7-yl-allyl)]}-2-but-3-ynyl-malonate (**42e**): To a slurry of sodium hydride (60%, 6.3 mg, 0.16 mmol) in 0.5 mL of distilled THF was added a solution of malonate ester (26 mg, 0.14 mmol) in 1 mL of THF at 0°C and stirred for 25 min. In another flask was added a solution of 3-[1,2-*cis*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-prop-2-en-1-ol (40 mg, 0.14 mmol) in 0.5 mL of distilled THF. To this solution was added *n*-butyllithium (1.6 M in hexane, 0.10 mL, 0.16 mmol) at -78°C and stirred for 30 min followed the addition of methanesulfonyl chloride (17 mg, 12 uL, 0.15 mmol). The solution was stirred for 2 h at –78°C. This solution was then transferred to the flask containing the malonate anion solution via cannulation at 0°C. About 10 mg of LiI was then added to the reaction mixture. After stirring at rt for 2 days, without workup the reaction mixture was submitted to flash chromatography eluting with 5% to 10% diethyl ether in petroleum ether to afford **42e** (44 mg, 0.098 mmol, 69%) as a colorless oil.
IR (film) cm^{-1}: 2931s, 2857s, 1741s, 1462w, 1438w, 1251m, 1206m, 1084s, 837s, 775m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.68 (d, *J*=15.0 Hz, 1H), 5.07 (dt, *J*=7.5, 15.0 Hz, 1H), 4.12 (dd, *J*=5.0, 7.5 Hz, 1H), 3.78 (s, 6H), 2.73 (m, 4H), 1.78 (m, 1H), 1.77 (s, 3H), 1.48 (m, 2H), 1.37 (m, 1H), 1.23 (m, 2H), 1.15 (m, 1H), 0.89 (s, 9H), 0.77 (dd, *J*=5.0, 6.0 Hz, 1H), 0.60 (dd, *J*=4.5, 9.0 Hz, 1H), 0.064 (s, 3H), 0.055 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.6, 142.3, 118.5, 94.2, 78.7, 70.5, 57.5, 52.7, 35.2, 31.4, 29.7, 28.2, 25.84, 23.5, 22.9, 19.1, 18.1, 16.3, 3.49, -4.19, -4.37; HRMS (EI+) Calc'd for $C_{25}H_{40}O_5Si$: 448.2645. Found: 448.2650.

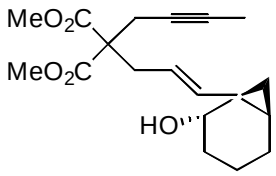


42f

Dimethyl 2-{3-[*trans*-1,2-(bicyclo[4.1.0]-2-*tert*-butyldimethylsilyloxy-hept-7-yl-allyl)]}-2-but-3-ynyl-malonate: To a slurry of sodium hydride (60%, 6.3 mg, 0.16 mmol) in 0.5 mL of distilled THF was added malonate ester (26 mg, 0.14 mmol) at 0°C. The mixture was stirred for 25 min. In another flask was added 3-[1,2-*trans*-2-(*tert*-butyldimethylsilyloxy)-bicyclo[4.1.0]hept-1-yl]-prop-2-en-1-ol (40 mg, 0.14 mmol) and 0.5 mL of distilled THF. To this solution was added *n*-butyllithium (1.6 M in hexane, 0.10 mL, 0.16 mmol) at -78°C. The mixture was stirred for 30 min followed by the addition of methanesulfonyl chloride (17 mg, 12

uL, 0.15 mmol). After being stirred for 2h at −78°C, this solution was transferred to the flask containing the malonate anion solution via cannulation at 0°C. To this mixture was added 10 mg of LiI. After stirring at rt for 2 days, the reaction mixture was submitted to flash chromatography eluting with 5% to 10% diethyl ether in petroleum ether to afford **42f** (48 mg, 0.11 mmol, 75%) as a colorless oil.

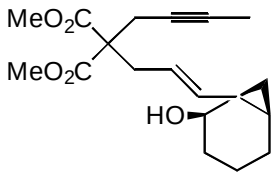
IR (film) cm^{-1}: 2952s, 2858s, 1741s, 1472w, 1458w, 1437m, 1329w, 1285w, 1251m, 1206s, 1074s, 1019m, 836m, 774m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.13 (d, *J*=15.0 Hz, 1H), 4.96 (dt, *J*=7.5, 15.0 Hz, 1H), 4.07 (t, *J*=4.0 Hz, 1H), 3.724 (s, 3H), 3.723 (s, 3H), 2.71 (t, *J*=7.0 Hz, 2H), 2.67 (t, *J*=2.5 Hz, 2H), 2.99 (m, 1H), 1.76 (t, *J*=2.5 Hz, 3H), 1.63 (m, 1H), 1.53 (m, 1H), 1.46 (m, 1H), 1.38 (m, 1H), 1.14 (m, 1H), 1.02 (m, 1H), 0.93 (s, 9H), 0.76 (dd, *J*=4.5, 9.5 Hz, 1H), 0.31 (t, *J*=5.0 Hz, 1H), 0.091 (s, 3H), 0.058 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.63, 170.61, 118.7, 78.7, 73.4, 69.2, 57.5, 52.5, 34.9, 29.6, 26.9, 25.9, 22.8, 22.7, 20.9, 18.2, 18.1, 15.3, 3.51, -4.59, -4.71; HRMS (EI+) Calc'd for $C_{25}H_{40}O_5Si$: 448.2645. Found: 448.2641.



42c

Dimethyl 2-{3-[*cis*-1,2-(bicyclo[4.1.0]-2-hydroxyl-hept-7-yl-allyl)]}-2-but-3-ynyl-malonate (**42c**): To a solution of **42e** (44 mg, 0.098 mmol) in 0.4 mL of distilled THF was added TBAF (1 M in THF, 0.30 mL, 0.30 mmol) at rt. After stirring for overnight, without workup the reaction mixture was purified via flash chromatography eluting with 10% to 60% diethyl ether in petroleum ether to afford **42c** (28 mg, 0.084 mmol, 86%) as a colorless oil.

IR (film) cm^{-1}: 3418b, 2933s, 2860m, 1738s, 1436m, 1288m, 1207s, 1039m; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.46 (d, *J*=15.9 Hz, 1H), 5.32 (dt, *J*=7.5, 15.3 Hz, 1H), 4.11 (dd, *J*=5.7, 9.3 Hz, 1H), 3.71 (s, 6H), 2.71 (m, 4H), 1.75 (t, *J*=2.4 Hz, 3H), 1.25 (m, 6H), 0.69 (m, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.6, 140.9, 120.7, 78.9, 73.3, 69.8, 57.7, 52.6, 35.3, 29.4, 28.8, 23.4, 23.2, 23.0, 21.0, 16.2, 3.49; HRMS (EI+) Calc'd for $C_{20}H_{30}O_5$: 350.2093. Found: 350.2094.



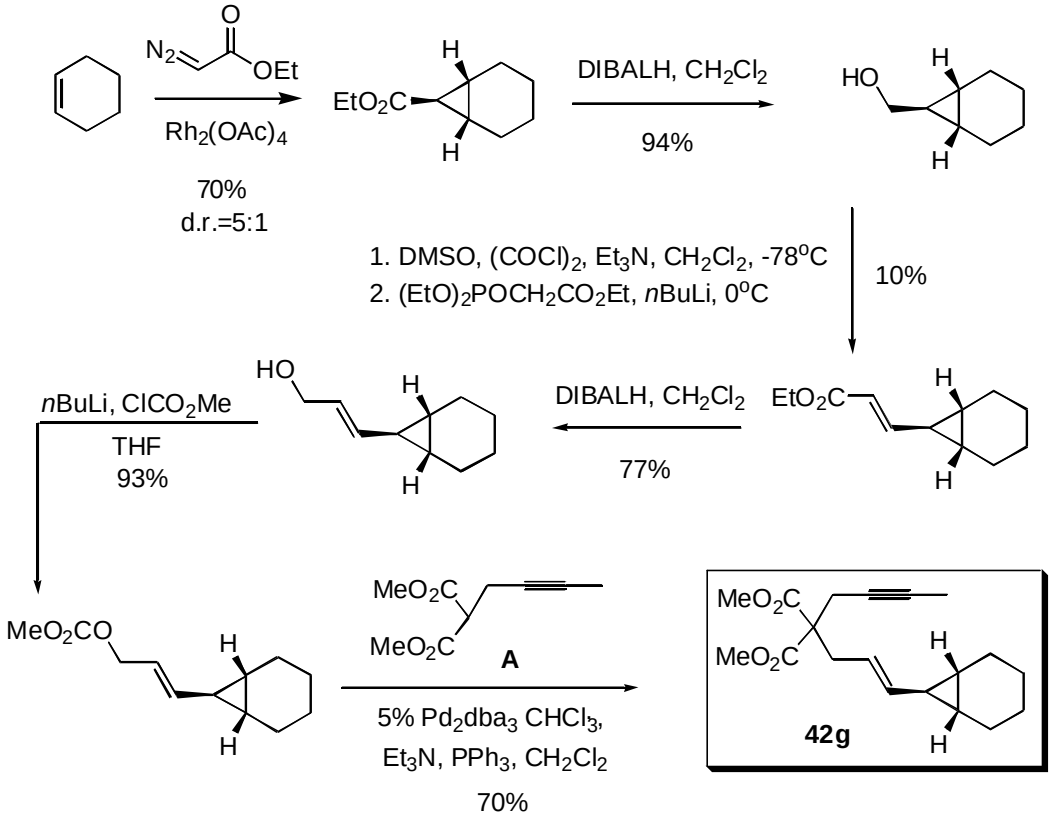
42d

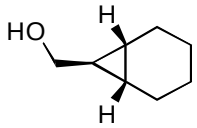
Dimethyl 2-{3-[*trans*-1,2-(bicyclo[4.1.0]-2-hydroxyl-hept-7-yl-allyl)]}-2-but-3-ynyl-malonate (**42d**): To a solution of **42f** (5.0 mg, 0.011 mmol) in 0.2 mL of distilled THF was added 1 M TBAF solution (55 uL) in THF at rt. The mixture was stirred overnight. Since most starting material did not react by TLC, the reaction mixture was heated at 50 °C for 4 h to give the complete desilylation. Without workup, the solution was directly purified by flash chromatography eluting with 50% diethyl ether in petroleum ether to afford **42d** (3.1 mg, 0.009 mmol, 81%) as a colorless oil.

IR (film) cm^{-1}: 3584b, 3002w, 2933s, 2859m, 1738s, 1436m, 1329w, 1288m, 1207s, 1059m, 973m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.74 (d, *J*=15.5 Hz, 1H), 5.40 (dt, *J*=7.5, 15.5 Hz, 1H),

4.19 (q, *J*=3.5 Hz, 1H), 3.753 (s, 3H), 3.751 (s, 3H), 2.75 (m, 4H), 2.06 (m, 1H), 1.93 (dd, *J*=1.0, 3.5 Hz, 1H), 1.78 (s, 3H), 1.61 (m, 2H), 1.40 (m, 1H), 1.21 (m, 1H), 0.95 (m, 1H), 0.61 (dd, *J*=4.5, 9.0 Hz, 1H), 0.42 (t, *J*=5.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 190.6, 138.9, 123.4, 79.0, 76.5, 73.2, 67.1, 57.7, 52.7, 35.3, 27.9, 27.5, 23.1, 22.3, 18.9, 18.4, 14.9; HRMS (EI+) Calc'd for $C_{20}H_{30}O_5$: 350.2093. Found: 350.2089.

42g:

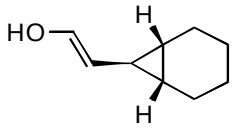




Bicyclo[4,1,0]hept-7-yl-methanol: To a solution of bicycle[4.1.0]heptane-7-ethylcarboxylate[40] (2.84 g, 16.9 mmol) in 30 mL of distilled dichloromethane was slowly added diisobutylaluminum hydride (33.8 mL, 33.8 mmol, 1.0 M in heptane) at -78 °C. The resulting slightly brown solution was warmed to rt and stirred overnight. To this solution was slowly added a 1M aqueous solution of Rochelle's salt (50 mL). The reaction mixture was stirred for 20 min before separation. The organic layer was washed with brine, and dried over magnesium sulfate. The mixture was then concentrated *in vacuo* and submitted to silica gel chromatography

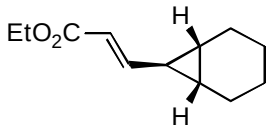
[40] a) Bendeddouche, K. C.; Benno, R.; Francoise, T. B.; Hamelin, J.; Benhaoua, H. *J. Chem. Res. Synop.* **2002**, *3*, 114. b) Salomon, R. G.; Salomon, M. F.; Kachinski, J. L. *J. Am. Chem. Soc*, **1977**, *99*, 1043.

eluting with 5% to 50% diethyl ether in petroleum ether to give bicyclo[4,1,0]hept-7-yl-methanol (2.0 g, 15.9 mmol, 94%) as a colorless oil as a 5:1 mixture of two diastereomers.
IR (film) cm^{-1}: 3334b, 3002m, 2926s, 2855s, 1449m, 1091w, 1024m, 763w; ^{1}H-NMR (300 MHz, $CDCl_3$): (ma*J*or isomer) δ 3.42(d, 2 H, *J*=6.9Hz), 1.87(m, 2 H), 1.62(m, 2 H), 1.20(m, 5H), 0.76(m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): (major isomer) δ 67.2, 26.1, 23.3, 21.4, 15.1; (minor isomer) δ 60.0, 22.3, 21.0, 18.9, 11.0; HRMS: Calc'd for $C_8H_{14}O$: 126.1045. Found: 126.1048.

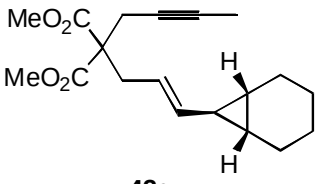


3-Bicyclo[4,1,0]hept-7-ylprop-2-en-1-ol: To DMSO (1.56 g, 1.42 mL, 20.0 mmol) in 4 mL of dichloromethane was added slowly at -78 °C, a solution of oxallyl chloride (1.22 g, 0.84 mL, 9.6 mmol) in 8 mL of dichloromethane. After 30 min, to this solution was added a solution of bicyclo[4,1,0]hept-7-yl-methanol (0.41 g, 8.0 mmol) in 4 mL of dichloromethane. After 30 min, to this mixture was added slowly triethylamine (3.24 g, 4.46 mL, 32.0 mmol). The mixture was warmed to 0 °C and stirred for another 30 min before it was recooled to -78 °C. To this mixture at -78 °C was then added a mixture of triethylphosphonoacetate (1.97 g, 1.75 mL, 8.8 mmol) and *n*-BuLi (6.86 mL, 1.4 M in hexane, 9.6 mmol), which was stirred at -10 °C for 30 min prior to the addition. The mixture was slowly warmed to rt over 6 h. Subsequent workup with 1N sodium bisulfate solution and brine gave a clear organic fraction, which was dried with magnesium sulfate. Concentration of the organic mixture *in vacuo* followed by purification by flash chromatography yielded 3-bicyclo[4,1,0]hept-7-yl-ethyl acrylate (155 mg, 0.8 mmol, 10%).

To 3-bicyclo[4,1,0]hept-7-yl-ethyl acrylate (188 mg, 0.97 mmol, combined material prepared by the above method twice) in 2 mL of distilled dichloromethane was slowly added diisobutylaluminum hydride (2.42 mL, 2.42 mmol, 1.0 M in hexane) at -78 °C. The resulting colorless solution was warmed to rt and stirred overnight. 1M saturated aqueous solution of Rochelle's salt was added slowly to quench the reaction solution. The reaction mixture was stirred for 20 min before separation. The organic layer was washed with brine, and dried over magnesium sulfate. The reaction mixture was then concentrated *in vacuo* and purified by silica gel chromatography eluting with 5 % to 35 % diethyl ether in petroleum ether to give alcohol 3-bicyclo[4,1,0]hept-7-ylprop-2-en-1-ol (116 mg, 0.76 mmol, 77 %) as a 3:1 mixture of two diastereomers.
IR (film): (mixture of two diastereomers) 3335b, 3008m, 2927s, 2855s, 1668w, 1448m, 1178w, 1126w, 1096w, 1073w, 1004m, 964m, 774w; ^{1}H-NMR (300 MHz, $CDCl_3$): (major isomer) δ 5.59(dt, 1H, *J*=6.3, 15.3Hz), 5.21(dd, 1H, *J*=9.0, 15.3Hz), 4.01(d, 2 H, *J*=6.3Hz), 1.88-0.92(m, 11H); ^{1}H-NMR (300 MHz, $CDCl_3$): (minor isomer) δ 5.81(dt, 1H, *J*=6.0, 15.0Hz), 5.59(dd, 1H, *J*=9.0, 15.0Hz), 4.10(d, 1H, *J*=6.0Hz), 1.88-0.92(m, 11H); ^{13}C-NMR (75 MHz, $CDCl_3$): (major isomer) δ 137.9, 125.0, 63.7, 26.4, 23.1, 21.3, 19.7; ^{13}C-NMR (75 MHz, $CDCl_3$): (minor isomer) δ 130.60, 130.55, 64.0, 22.4, 21.8, 19.2, 14.3; HRMS: Calc'd for $C_{10}H_{16}O$: 152.1201. Found: 152.1202.

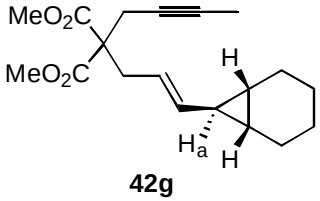


3-Bicyclo[4,1,0]hept-7-yl-allyl methyl carbonate: To a solution of 3-bicyclo[4,1,0]hept-7-ylprop-2-en-1-ol (67 mg, 0.44 mmol) in 1.0 mL of distilled THF was added *n*-butyllithium (1.6 M in hexane, 0.31 mL, 0.49 mmol) at -78^{o}C and stirred at this temperature for 30 min. To this mixture was added methyl chloroformate (50 mg, 0.04 mL, 0.53 mmol) at and the solution was stirred at -78^{o}C for 1 h. The reaction solution was diluted with diethyl ether (3 mL), washed with water (2 mL). The organic layer was washed with brine and dried with magnesium sulfate. After removal of the solvent *in vacuo*, flash chromatography of the residue eluting with 5 % to 15% diethyl ether in petroleum ether gave carbonate bicyclo[4,1,0]hept-7-yl-allyl methyl carbonate (86 mg, 0.41 mmol, 93 %) as a 2:1 mixture.
IR (film) cm^{-1}: 2956s, 2990s, 2858s, 1740s, 1472w, 1370m, 1239s, 1094s, 1019m, 938w, 838s, 776s; ^{1}H-NMR (300 MHz, $CDCl_3$): (major isomer): δ 5.55 (dt, 1H, *J*=6.6, 15.3 Hz), 5.34 (dd, 1H, *J*=9.0, 15.0 Hz), 4.52 (d, 2 H, *J*=6.0 Hz), 3.75 (s, 3H), 1.85-0.88 (m, 11H); ^{1}H-NMR (300 MHz, $CDCl_3$): (minor isomer): δ 5.74 (m, 2 H), 4.60 (d, 2 H, *J*=5.7Hz), 3.76 (s, 3H), 1.85-0.88 (m, 11H); ^{13}C-NMR (75 MHz, $CDCl_3$): (major isomer) δ 155.7, 142.2, 119.0, 68.8, 54.6, 38.9, 26.6, 21.3, 20.0; ^{13}C-NMR (75 MHz, $CDCl_3$): (minor isomer) δ 155.7, 135.2, 124.5, 68.9, 34.8, 30.3, 25.6, 23.0, 22.3; HRMS: Calc'd for $C_{12}H_{18}O_3$: 210.1256. Found: 210.1258.



42g

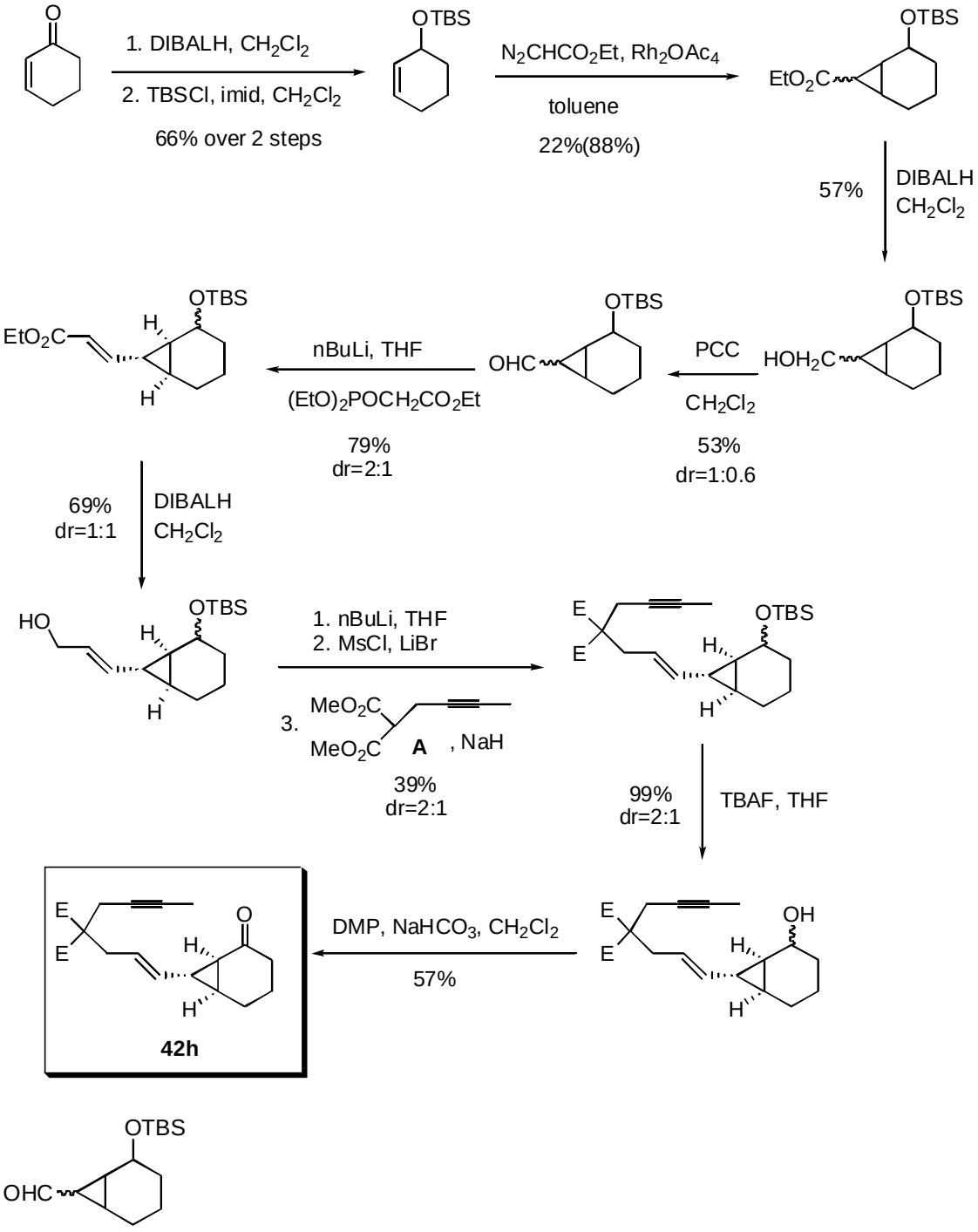
Dimethyl-2-(3-Bicyclo[4,1,0]hept-7-yl-allyl)-2-but-2ynyl-malonate (**42g**): To a degassed flask (refilled with argon) containing a solution of malonate ester **A** (26 mg, 0.14 mmol) in 0.5 mL of distilled dichloromethane was added palladium dibenzylideneacetone chloroform catalyst (7.5 mg, 0.007 mmol) and triphenylphosphine (11 mg, 0.04 mmol). The resulting orange solution was stirred at rt for 5 min. To this solution was added a solution of bicyclo[4,1,0]hept-7-yl-allyl methyl carbonate (30 mg, ds=2:1, 0.14 mmol) in 0.5 mL of dichloromethane followed by triethylamine (16 mg, 0.02 mL, 0.16 mmol) to afford an orange solution. The solution was stirred at rt for 6 h. After 6 h, without workup the solution was purified by flash chromatography eluting with 5%-10% diethyl ether in petroleum ether to give **42g** (32 mg, 0.10 mmol, 70 %, quantitative yield brsm) as a colorless oil as a single diastereomer. The minor carbonate gave isomerized carbonate and could not be alkylated to the malonate ester under the given condition.
IR (film) cm^{-1}: 3004w, 2929s, 2857m, 1740s, 1664w, 1438m, 1288m, 1204s, 1125w, 1098w, 1073w, 1026w, 999w, 968w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.13 (m, *J*=7.5, 12.0 Hz, 2 H), 3.71 (s, 6 H), 2.71 (d, *J*=2.4 Hz, 2 H), 2.67 (d, *J*=6.3 Hz, 2 H), 1.82 (m, 2 H), 1.74 (t, *J*=2.4 Hz, 3 H), 1.62 (m, 2 H), 1.41 (m, 1 H), 1.19 (m, 5 H), 1.02 (dt, *J*=4.8, 7.5 Hz, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.7, 139.6, 119.0, 78.7, 73.5, 57.6, 52.5, 39.0, 35.4, 26.7, 25.7, 23.1, 22.9, 21.4, 19.5, 14.1, 3.5; HRMS: Calc'd for $C_{19}H_{26}O_4$: 318.1831. Found: 318.1831.



42g

δ_a= 1.02 ppm, *J* = 4.8 Hz

Preparation of **42h**:



2-(tert-Butyl-dimethyl-silanyloxy)-bicyclo[4.1.0]heptane-7-carbaldehyde: To a solution of cyclohexenone (4.81 g, 50 mmol) in 40 mL dichloromethane was added DIBALH (55 mL, 1 M in hexane, 55 mmol) at 0 °C. The solution was warmed to rt and stirred 2 h. The resulting

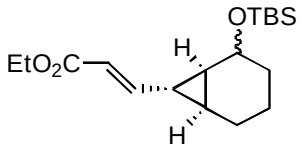
solution was quenched with a saturated solution of Rochelle's salt (200 mL). The aqueous layer was extracted with diethyl ether (3 x 200 mL). The organic fractions were dried with magnesium sulfate and concentrated *in vacuo* to afford 2-cyclohexen-1-ol (3.68 g, 37.5 mmol, 75%) as a colorless oil.

Treatement of 2-cyclohexen-1-ol (1.10 g, 11.2 mmol) with TBSCl (1.86 g, 12.3 mmol), imidazole (0.91 g, 13.4 mmol) and 10 mL of dichloromethane afforded 2-cyclohexen-1-*tert*-butyldimethylsilyl ether (8.57 g, 40.4 mmol, 88%).

The cyclopropanation procedure followed reference 11. 2-Cyclohexen-1-*tert*-butyldimethylsilyl ether (2.12 g, 10.0 mmol), ethyl diazoacetate (1.26 g, 11.0 mmol), rhodium acetate dimer (26 mg, 0.1 mmol) afforded 2-*tert*-butyldimethylsilyoxy-bicyclo[4.1.0]heptane-7-ethylcarboxylate (0.65 g, 2.18 mmol, 22%, 88% brsm).

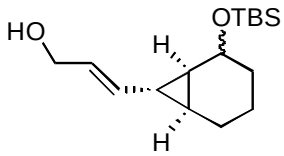
The reduction of 2-*tert*-butyldimethylsilyoxy-bicyclo[4.1.0]heptane-7-ethylcarboxylate (0.98 g, 3.29 mmol) by DIBALH (6.6 mL, 1 M in hexane, 6.6 mmol) in dichloromethane afforded 2-*tert*-butyldimethylsilyoxy-bicyclo[4.1.0]heptane-7-methanol (0.43 g, 1.87 mmol, 57%).

Subsequent oxidation of 2-*tert*-butyldimethylsilyoxy-bicyclo[4.1.0]heptane-7-methanol (0.43g, 1.87 mmol) by PCC (605 mg, 2.81 mmol) gave 2-*tert*-butyldimethylsilyoxy-bicyclo[4.1.0]heptane-7-carboxaldehyde (228 mg, 0.99 mmol, 53%) as a 1:0.6 mixture of two diastereomers.



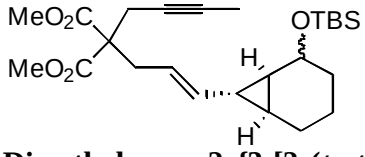
3-[2-(*tert*-Butyldimethylsilyloxy-bicyclo[4.1.0]hept-7-yl]-acrylic acid ethyl ester: To a solution of triethyl acetylphosphonoacetate (244 mg, 1.09 mmol) in 2 mL of THF was added *n*-butyllithium (0.83 mL, 1.19 mmol, 1.43 M in hexane) at 0°C. The reaction mixture was stirred for 30 min. To this resulting solution was added 2-*tert*-butyldimethylsilyoxy-bicyclo[4.1.0]heptane-7-carboxaldehyde (228 mg, 0.99 mmol) in 2 mL of THF at 0 °C. The mixture was warmed to rt slowly and stirred overnight. Without workup, purification by column chromatography eluting with 5% diethyl ether in petroleum ether afforded 3-[2-(*tert*-butyldimethylsilyloxy-bicyclo[4.1.0]hept-7-yl]-acrylic acid ethyl ester (0.25 g, 0.78 mmol, 79%) as a colorless oil.

IR (film) cm^{-1}: 2934s, 2857s, 1716s, 1644s, 1472m, 1463m, 1448w, 1390w, 1367m, 1315m, 1257s, 1209m, 1155s, 1086s, 1043s, 1007s, 979m, 941m, 908w, 836s, 775s, 709w, 669w; Major isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.46 (dd, *J*=9.5, 18.5 Hz, 1H), 5.78 (d, *J*=17.5 Hz, 1H), 4.22 (m, 1H), 4.17 (m, 2H), 1.86 (m, 1H), 1.67 (m, 1H), 1.28-1.57 (m, 5H), 1.27 (m, 3H), 1.22 (m, 1H), 1.01 (m, 1H), 0.88 (m, 9H), 0.05 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 166.7, 153.1, 117.2, 67.3, 60.0, 31.1, 30.4, 25.8, 25.7, 22.8, 22.2, 16.2, 14.2, -4.80, -4.83; Minor isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.46 (dd, *J*=9.5, 13.5 Hz, 1H), 5.81 (d, *J*=17.0 Hz, 1H), 4.17 (m, 2H), 3.95 (m, 1H), 1.86 (m, 1H), 1.67 (m, 1H), 1.28-1.57 (m, 4H), 1.27 (m, 3H), 1.22 (m, 1H), 1.19 (m, 2H), 0.88 (m, 9H), 0.05 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 166.9, 153.6, 117.3, 65.9, 59.8, 31.0, 29.4, 25.8, 24.13, 24.07, 22.4, 19.2, 18.1, -4.47, -4.86; HRMS (EI+) Calc'd for $C_{18}H_{32}O_3Si$: 324.2121. Found: 324.2122.



3-[2-(*tert*-Butyldimethylsilyloxy-bicyclo[4.1.0]hept-7-yl]-prop-2-en-1-ol: To a solution of 3-[2-(*tert*-butyldimethylsilyloxy-bicyclo[4.1.0]hept-7-yl]-acrylic acid ethyl ester (0.25 g, 0.78 mmol) in 4 mL of dichloromethane at 0°C was added DIBALH (1.64 mL, 1.64 mmol, 1 M in hexane). The solution was warmed to rt and stirred for overnight. The resulting solution was quenched with water (2 mL). Without further workup, the mixture was directly purified over silica gel chromatography to afford 3-[2-(*tert*-butyldimethylsilyloxy-bicyclo[4.1.0]hept-7-yl]-prop-2-en-1-ol (151 mg, 0.54 mmol, 69%) as a colorless oil.

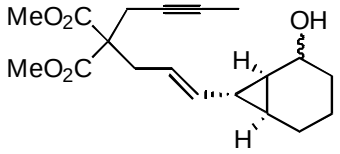
IR (film) cm^{-1}: 3343b, 3006w, 2834s, 2857s, 1666w, 1472m, 1462m, 1389w, 1361w, 1253m, 1083s, 1043m, 1006s, 962m, 012w, 876w, 837s, 774s, 669w; Two isomers: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.63 (m, 2H), 5.24 (m, 2H), 4.17 (m, 1H), 4.04 (m, 4H), 3.95 (m, 1H), 1.83 (m, 2H), 0.95-1.66 (m, 9H), 0.88 (m, 9H), 0.06 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 137.1, 136.7, 126.0, 125.7, 67.6, 66.6, 63.8, 63.7, 31.2, 31.1, 28.3, 27.5, 25.91, 25.87, 24.8, 23.2, 22.6, 22.4, 21.9, 20.5, 19.8, 18.24, 18.19, 16.3, -4.4, -4.7.; HRMS (EI+) Calc'd for $C_{16}H_{30}O_2Si$: 282.2015. Found: 282.2016.



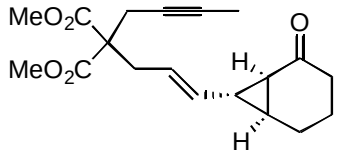
Dimethyl 2-{3-[2-(*tert*-butyldimethylsilyloxy-bicyclo[4.1.0]hept-7-yl]-allyl}-but-2-ynyl-malonate: To a slurry sodium hydride (60%, 24 mg, 0.59 mmol) in 0.5 mL of distilled THF was added a solution of malonate ester **A** (99 mg, 0.54 mmol) in 0.5 mL of THF at 0°C and stirred for 25 min. To another flask was added 3-[2-(*tert*-butyldimethylsilyloxy-bicyclo[4.1.0]hept-7-yl]-prop-2-en-1-ol (151 mg, 0.54 mmol) in 0.5 mL of distilled THF. To this solution was added *n*-butyllithium (0.42 mL, 0.16 mmol, 1.43 M in hexane) at -78°C and stirred for 30 min followed the addition of methanesulfonyl chloride (68 mg, 46 uL, 0.59 mmol). The solution was stirred for 2 h at –78°C followed by the addition of about 20 mg of lithium bromide. The resulting solution was then transferred to the flask containing the malonate anion solution via cannulation at 0°C. After stirring at rt overnight, without workup the reaction mixture was submitted to flash chromatography eluting with 5% to 10% diethyl ether in petroleum ether to afford dimethyl 2-{3-[2-(*tert*-butyldimethylsilyloxy-bicyclo[4.1.0]hept-7-yl]-allyl}-but-2-ynyl-malonate (95 mg, 0.21 mmol, 39%) as a colorless oil.

IR (film) cm^{-1}: 2952s, 2988s, 2857m, 1741s, 1642w, 1438m, 1361w, 1328w, 1286w, 1252m, 1210s, 1082s, 1043m, 1006w, 965w, 836m, 775m, 668w; Major isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.21 (dt, *J*=7.0, 15.5 Hz, 1H), 5.11 (dd, *J*=8.0, 15.0 Hz, 1H), 3.92 (m, 1H), 3.72 (s, 6H), 2.73 (m, 4H), 1.76 (d, *J*=2.5 Hz, 3H), 0.93-1.82 (m, 9H), 0.92 (m, 9H), 0.08 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.60, 170.58, 138.5, 119.8, 78.6, 73.3, 67.9, 57.5, 52.5, 35.3, 31.4, 28.1, 25.90, 24.9, 22.9, 22.4, 20.3, 16.5, 3.45, -4.75, -4.81; Minor isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.19 (dt, *J*=7.0, 15.5 Hz, 1H), 5.11 (dd, *J*=8.0, 15.0 Hz, 1H), 4.17 (m, 1H), 3.73 (s, 6H), 2.73 (m, 4H), 1.75 (d, *J*=1.5 Hz, 3H), 0.93-1.82 (m, 9H), 0.92 (m, 9H), 0.08 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.57, 138.9, 119.9, 78.5, 73.4, 66.7, 52.6, 52.5, 35.2, 31.1, 27.3,

25.87, 23.4, 22.7, 22.6, 21.6, 19.9, 20.3, 19.9, 18.3, -4.40, -4.77; HRMS (EI+) Calc'd for $C_{25}H_{40}O_5Si$: 448.2645. Found: 448.2648.



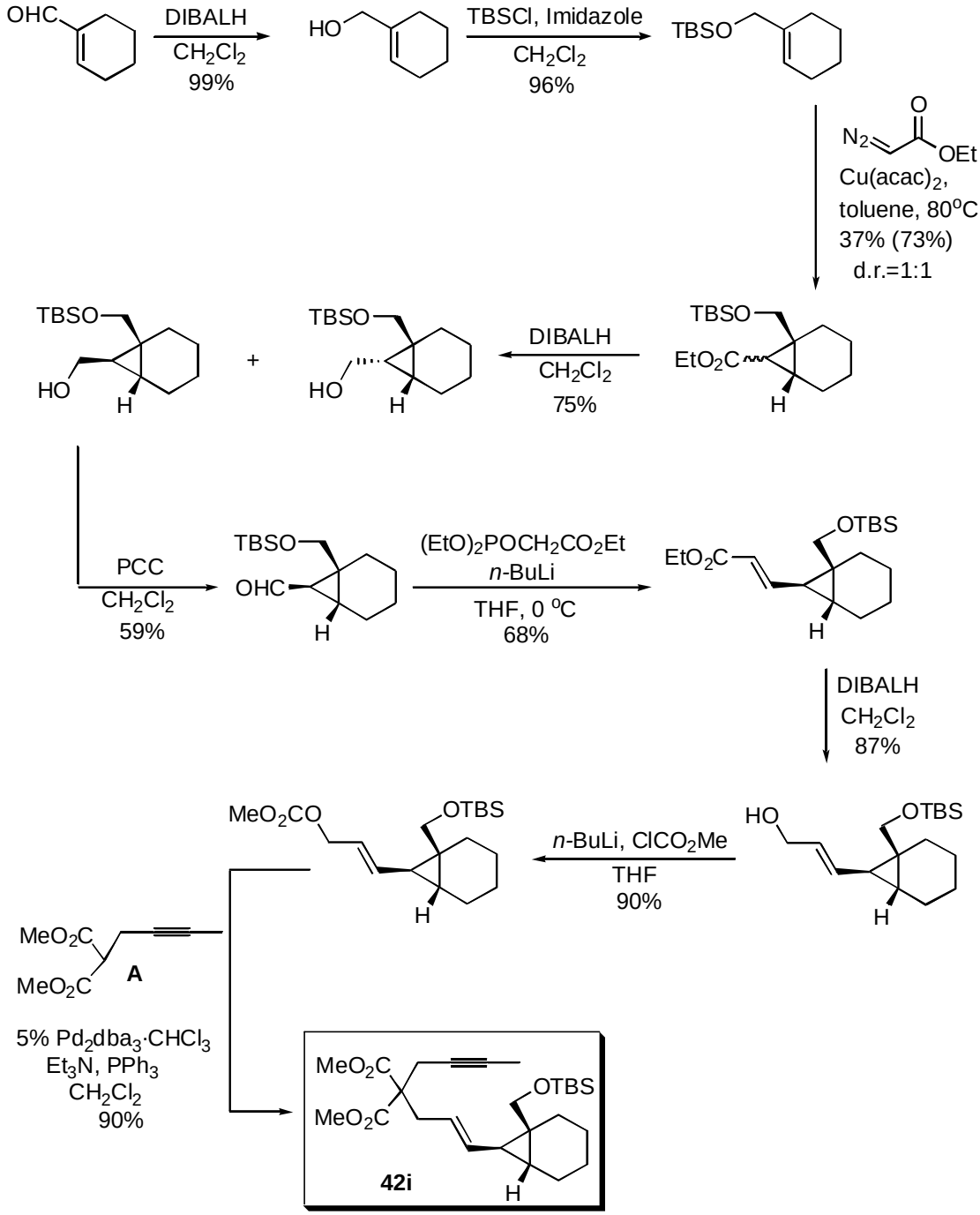
Dimethyl 2-but-2-ynyl-2-[3-(2-hydroxy-bicyclo[4.1.0]hept-7-yl]-allyl}-malonate: To a solution of silyl ether dimethyl 2-{3-[2-(*tert*-butyldimethylsilyloxy-bicyclo[4.1.0]hept-7-yl]-allyl}-but-2-ynyl-malonate (84 mg, 0.19 mmol) in 1 mL of THF was added TBAF (0.47 mL, 0.47 mmol, 1M in THF) at rt. The solution was stirred for 8 h and without workup chromatographed directly eluting with 5% to 30% diethyl ether in petroleum ether to afford alcohol dimethyl 2-but-2-ynyl-2-[3-(2-hydroxy-bicyclo[4.1.0]hept-7-yl]-allyl}-malonate (67 mg, 0.20 mmol, ~100%) as a colorless oil.
IR (film) cm^{-1}: 3544b, 3418b, 3002w, 2931s, 2857m, 1738s, 1663w, 1437s, 1288s, 1210s, 1069m, 1002w, 967m, 857w, 777w; Major isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.21 (m, 2H), 4.05 (m, 1H), 3.73 (s, 6H), 2.72 (m, 4H), 2.42 (m, 1H), 1.88 (m, 2H), 1.76 (d, *J*=3.0 Hz, 3H), 0.95-1.66 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.6, 138.1, 120.3, 78.7, 73.3, 66.4, 53.7, 52.6, 35.2, 30.4, 27.2, 25.3, 22.9, 22.4, 20.8, 19.7, 3.46; Minor isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.21 (m, 2H), 4.18 (m, 1H), 3.73 (s, 6H), 2.71 (m, 4H), 2.42 (m, 1H), 1.88 (m, 2H), 1.76 (d, *J*=3.0 Hz, 3H), 0.95-1.66 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.6, 138.0, 120.6, 78.7, 73.3, 66.8, 64.9, 57.5, 43.4, 33.0, 32.8, 30.0, 29.5, 25.9, 22.6, 18.9, 14.4; HRMS (EI+) Calc'd for $C_{19}H_{26}O_5$: 334.1780. Found: 334.1782.



42h

Dimethyl 2-but-2-ynyl-2-[3-(1,2-*trans*-2-oxo-bicyclo[4.1.0]hept-7-yl]-allyl}-malonate (**42h**): To a solution of dimethyl 2-but-2-ynyl-2-[3-(2-hydroxy-bicyclo[4.1.0]hept-7-yl]-allyl}-malonate (67 mg, 0.20 mmol) in 1 mL of dichloromethane were added sodium bicarbonate (25 mg, 0.30 mmol) and Dess-Martin periodinane (102 mg, 0.24 mmol) at rt. The resulting mixture was stirred at rt for 4 h. Without workup, the mixture was chromatographed eluting with 5% to 15% diethyl ether in petroleum ether to afford ketone **42h** (38 mg, 0.11 mmol, 57%) as a colorless oil.
IR (film) cm^{-1}: 3005w, 2953s, 2860w, 1738s, 1689s, 1437s, 1327m, 1288s, 1242s, 1212s, 1149m, 1130m, 1066m, 1030w, 999w, 968m, 900m, 876w, 746w, 681w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.38 (dt, *J*=7.5, 15.3 Hz, 1H), 5.11 (dd, *J*=8.4, 15.3 Hz, 1H), 3.702 (s, 3H), 3.698 (s, 3H), 2.67 (m, 4H), 1.70-2.31 (m, 9H), 1.72 (t, *J*=2.4 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 206.9, 170.4, 134.4, 124.0, 78.9, 73.1, 57.2, 52.6, 36.8, 35.2, 34.4, 26.5, 25.1, 23.0, 20.9, 18.5, 3.43; HRMS (EI+) Calc'd for $C_{19}H_{24}O_5+H^+$: 333.1702. Found: 333.1689.

42i: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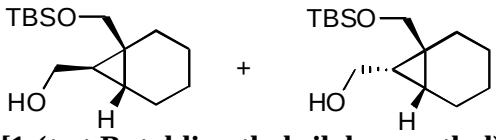
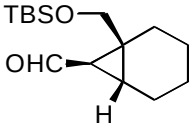
99%
HO
TBSCl, Imidazole
CH_2Cl_2
96%
TBSO
O
N_2
OEt
$Cu(acac)_2$,
toluene, 80°C
37% (73%)
d.r.=1:1
TBSO
EtO_2C
H
DIBALH
CH_2Cl_2
75%
TBSO
HO
H
+
PCC
CH_2Cl_2
59%
OHC
$(EtO)_2POCH_2CO_2Et$
n-BuLi
THF, 0 °C
68%
EtO_2C
OTBS
DIBALH
CH_2Cl_2
87%
HO
n-BuLi, $ClCO_2Me$
THF
90%
MeO_2CO
MeO_2C
MeO_2C
A
5% $Pd_2dba_3 \cdot CHCl_3$
Et_3N, PPh_3
CH_2Cl_2
90%
42i



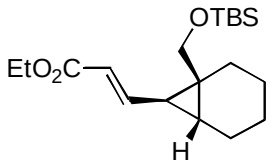
[1-(*tert*-Butyldimethyl-silyloxymethyl)-bicyclo[4.1.0]hept-7-yl]-methanol: To a mixture of *tert*-butyl-(cyclohex-1-enylmethoxy)-dimethyl-1-silane (370 mg, 1.64 mmol) and $Cu(acac)_2$ (21 mg, 0.08 mmol) was slowly added a solution of ethyl diazoacetate (225 mg, 0.21 mL, 1.97 mmol) in 5 mL of toluene at 80°C slowly under nitrogen over 4h. The mixture was heated at this temperature overnight. After removal of the solvent in vacuo, the residue was purified by flash chromatography eluting with 5% diethyl ether in petroleum ether to give propionic acid 1-(*tert*-butyldimethylsiloxymethyl)-bicyclo[4.1.0]hept-7-yl ester (190 mg, 0.61 mmol, 37%, 73% brsm) as a mixture of two diastereomers (d.r.=1:1). To a solution of 1-(*tert*-butyldimethylsiloxymethyl)-bicyclo[4.1.0]hept-7-yl ester (179 mg, 0.57 mmol) in 5 mL of distilled dichloromethane at -78 °C was added diisobutylaluminum hydride (1.5 mL, 1.0 M in heptane) slowly. The resulting colorless solution was warmed to rt and stirred overnight. To this mixture was then added 5 mL of 1 M aqueous solution of Rochelle's salt. The mixture was stirred for 20 min before separation. The organic layer was washed with brine, dried over magnesium sulfate, and concentrated *in vacuo*. The residue was purified using silica gel chromatography eluting with 5 % to 20 % diethyl ether in petroleum ether to give [1-(*tert*-butyldimethyl-silyloxymethyl)-bicyclo[4.1.0]hept-7-yl]-methanol (116 mg, 0.43 mmol, 75%, 1:1) as a mixture of two diastereomers.

IR (film) cm^{-1}: 3421b, 2930s, 2858s, 1472w, 1257m, 1120w, 1068m, 1048s, 939w, 836s, 777m, 668m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.98 (dd, 1 H, *J*=5.0, 12.5 Hz), 3.90 (d, 1 H, *J*=11.0 Hz), 3.32 (d, 1 H, *J*=10.5 Hz), 3.23 (dd, 1 H, *J*=10.5, 12.5 Hz), 1.93 (m, 1 H), 1.78 (m, 1 H), 1.64 (m, 1 H), 1.59 (m, 1 H), 1.28 (m, 4 H), 1.93 (m, 1H), 1.21(s, 9H), 0.89(m, 1H), 0.72 (m, 1 H), 0.09 (ds, 6 H); ^{13}C-NMR (300 MHz, $CDCl_3$): δ 30.0, 29.7, 25.8, 25.3, 22.8, 21.4, 21.2, 21.0, 20.9, 18.2, -5.4, -5.5; HRMS: Calc'd for $C_{15}H_{30}O_2Si$: 270.2015. Found: 270.2014.

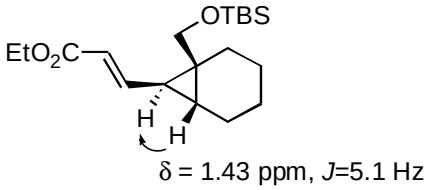


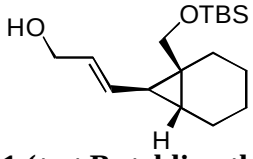
1-(*tert*-Butyldimethylsilyloxymethyl)-bicyclo[4.1.0]heptane-7-carboxyaldehyde: To a solution of [1-(*tert*-butyldimethyl-silyloxymethyl)-bicyclo[4.1.0]hept-7-yl]-methanol (45 mg, 0.17 mmol) in 1 mL of distilled methylenechloride was added pyridiniumchlorochromate (72 mg, 0.33 mmol) at 0°C. The solution was stirred at rt for 2 h. The resulting solution was filtered through cotton and washed thoroughly with dichloromethane. The resulting solution was concentrated *in vacuo* and the residue was separated by chromatography eluting with 5 % to 15 % diethyl ether in petroleum ether to afford 1-(*tert*-butyldimethylsilyloxymethyl)-bicyclo[4.1.0]heptane-7-carboxyaldehyde as a slightly yellow oil (27 mg, 0.10 mmol, 59 %).

IR (film) cm^{-1}: 2931s, 2858s, 2723w, 1700s, 1472w, 1256m, 1207w, 1084s, 1006w, 838s, 776m, 668m; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.35 (d, 1H, *J*=5.4 Hz), 3.78 (d, 1 H, *J*=10.5 Hz), 3.57(d, 1H, *J*=10.8 Hz), 1.94 (m, 6 H), 1.26 (m, 4 H), 0.86 (s, 9 H), 0.022 (s, 3 H), 0.008 (s, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 201.2, 66.5, 40.3, 37.0, 28.0, 26.4, 25.8, 22.6, 20.9, 20.8, 18.2, -5.43; HRMS: Calc'd for $C_{15}H_{28}O_2Si$: 268.1859. Found: 268.4671.



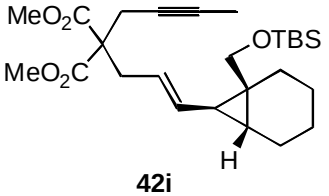
1-(*tert*-Butyldimethylsilyloxymethyl)-bicyclo[4.1.0]hept-7-yl]-acrylic acid ethyl ester: To a solution of distilled ethyl phosphonoacetate (25 mg, 0.11 mmol) in 0.3 mL of distilled THF was added *n*-butyllithium (1.6 M, 0.075 mL, 0.12 mmol) at 0 ^{o}C. The resulting pale yellow solution was stirred at 0^{o}C for 15 min. To this solution was added a solution of 1-(*tert*-butyldimethylsilyloxymethyl)-bicyclo[4.1.0]heptane-7-carboxyaldehyde (27 mg, 0.10 mmol) in 0.2 mL of distilled THF via cannulation. The resulting yellow solution was stirred at rt for 2.5 h. The solution was then concentrated *in vacuo* and submitted to silica gel chromatography (eluting with 5%-15% diethyl ether in petroleum ether) to afford 1-(*tert*-butyldimethylsilyloxymethyl)-bicyclo[4.1.0]hept-7-yl]-acrylic acid ethyl ester (23 mg, 0.068 mmol, 68%) as a colorless oil.
IR (film) cm^{-1}: 2930s, 2857s, 1716s, 1638m, 1464w, 1258m, 1155m, 1128m, 1082m, 1044w, 837m, 776w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.76 (dd, *J*=10.5, 15.3 Hz, 1H), 5.83 (d, *J*=15.3 Hz, 1H), 4.15 (q, *J*=6.9 Hz, 2 H), 3.64 (d, *J*=10.5 Hz, 1H), 3.48 (d, *J*=10.5 Hz, 1H), 1.59-1.92 (m, 4H), 1.43 (dd, *J*=5.1, 10.5 Hz, 1H), 1.26 (m, 8H), 0.87 (s, 9H), 0.031 (s, 3H), 0.021 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 166.7, 151.1, 119.0, 67.9, 59.8, 32.4, 31.9, 27.9, 26.9, 25.9, 22.9, 21.2, 21.1, 18.2, 14.4, -5.37, -5.48; HRMS: Calc'd for $C_{19}H_{34}O_3Si$: 338.2277. Found: 338.2280.
nOe study:





1-(*tert*-Butyldimethylsilyloxymethyl)-bicyclo[4.1.0]hept-7-yl]-hept-7-yl]-prop-2-en-1-ol: To a solution of 1-(*tert*-butyldimethylsilyloxymethyl)-bicyclo[4.1.0]hept-7-yl]-acrylic acid ethyl ester (66mg, 0.19mmol) in 0.3 mL of distilled dichloromethane was added diisobutylaluminum hydride (1.0M in hexane, 0.40 mL, 0.40mmol) at 0 ^{o}C slowly. The resulting colorless solution was warmed to rt and stirred overnight. To this solution was added 3 mL of 1 M aqueous solution of Rochelle's salt to quench the reaction solution. The resulting mixture was stirred for 30 min before the phase separation. The organic layer was washed with brine, dried over magnesium sulfate, and concentrated *in vacuo*. The residue was submitted to silica gel chromatography eluting with 5 % to 35 % diethyl ether in petroleum ether to give 1-(*tert*-butyldimethylsilyloxymethyl)-bicyclo[4.1.0]hept-7-yl]-hept-7-yl]-prop-2-en-1-ol (50 mg, 0.17 mmol, 87 %) as a colorless oil.
IR (film) cm^{-1}: 3355b, 2929s, 2856s, 1654w, 1472m, 1388w, 1256m, 1080s, 1006m, 837s, 775w, 663m; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.69 (dt, *J*=6.0, 15.3 Hz, 1H), 5.50 (dd, *J*=9.0, 15.3 Hz, 1H), 4.07 (d, *J*=6.0 Hz, 2H), 3.53 (d, *J*=10.5 Hz, 1H), 3.44 (d, *J*=10.5 Hz, 1H), 1.80 (m, 2H), 1.67 (m, 2H), 1.25 (m, 4H), 0.95 (m, 2H), 0.88 (s, 9H), 0.02 (s, 6H); ^{13}C-NMR (75 MHz,

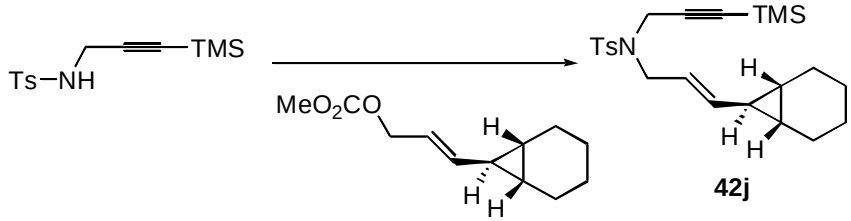
$CDCl_3$): δ 133.9, 128.0, 68.1, 64.0, 30.7, 28.7, 27.6, 25.8, 24.1, 23.0, 21.35, 21.28, -5.4, -5.5; HRMS: Calc'd for $C_{17}H_{32}O_2Si$: 296.2172. Found: 296.2172.



42i

Dimethyl 2-{3-[1-(*tert*-butyldimethylsilyloxymethyl)-bicyclo[4.1.0]hept-7-yl]-allyl}-2-but-2-ynyl-malonate (**42i**): To a solution of 1-(*tert*-butyldimethylsilyloxymethyl)-bicyclo[4.1.0]hept-7-yl]-hept-7-yl]-prop-2-en-1-ol (66 mg, 0.22 mmol) in 1 mL of distilled THF was added *n*-butyllithium (1.6 M, 0.17 mL, 0.27 mmol) at −78°C. The resulting solution was stirred for 30 min. To this solution was added methylchloroformate (25 mg, 0.27 mmol, 21 uL) at −78°C. The resulting solution was stirred at −78°C for 20 min and then warmed to rt. After stirring at rt for 3 h, the mixture was diluted with diethyl ether, washed with water and brine, and dried over magnesium sulfate. Without flash chromatography, after the removal of solvent *in vacuo* the liquid residue **42i** (71 mg, 0.20 mmol, 90 %) was directly submitted to next reaction.
IR (film) cm^{-1}: 2929s, 2857s, 1741s, 1438w, 1285w, 1251m, 1202s, 1079s, 970w, 838s, 776m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.39 (dd, *J*=8.5, 15.0 Hz, 1 H), 5.24 (dt, *J*=7.5, 15.0 Hz, 1 H), 3.74 (s, 6 H), 3.45 (d, *J*=5.0 Hz, 2 H), 2.74 (m, 4 H), 1.85 (m, 2 H), 1.76 (t, *J*=2.5 Hz, 3 H), 1.63 (m, 2 H), 1.23 (m, 6 H), 0.90 (s, 9 H), 0.04 (s, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.6, 135.3, 122.0, 78.6, 73.4, 68.0, 57.4, 52.6, 35.4, 30.1, 28.3, 27.4, 25.9, 23.9, 23.1, 22.8, 21.4, 18.3, 3.48, -5.31, -5.32; HRMS: Calc'd for $C_{26}H_{42}O_5Si$: 462.2802. Found: 462.6942.

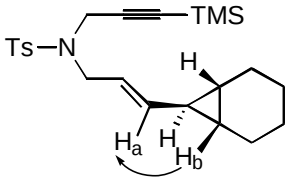
42j:



42j

***N*-(3-Bicyclo[4.1.0]hept-7-yl-allyl)-*N*-(3-trimethylsilylprop-2-ynyl)-toluenesulfonamide** (**42j**): To a degassed flask (refilled with argon) containing a solution of 4-trimethylsilyl-3-propargyl-*p*-toluenesulfonamide (48 mg, 0.17 mmol) in 0.5 mL of distilled dichloromethane was added palladium dibenzylideneacetone chloroform catalyst (9 mg, 0.009 mmol), triphenylphosphine (13 mg, 0.05 mmol). The resulting orange solution was stirred at rt for 5 min. To this solution was added a solution of carbonate (36 mg, 0.17 mmol) in 0.5 mL of dichloromethane followed by triethylamine (19 mg, 26 uL, 0.19 mmol) to afford an orange solution. The solution was stirred at rt for 10 h. After 10 h, without workup the solution was submitted to flash chromatography eluting with 5%-10% diethyl ether in petroleum ether to give a colorless oil as a mixture of 1.8 : 1 separable regioisomers with the major isomer being **42j** (37 mg, 0.10 mmol, 61 %).
IR (film) cm^{-1}: 3008w, 2928s, 2855m, 2177w, 1662w, 1598w, 1495w, 1449w, 1350s, 1250m, 1102s, 1093m, 1002m, 897m, 845s, 814m, 761m, 73 6w, 666m, 642w; ^{1}H-NMR (500 MHz,

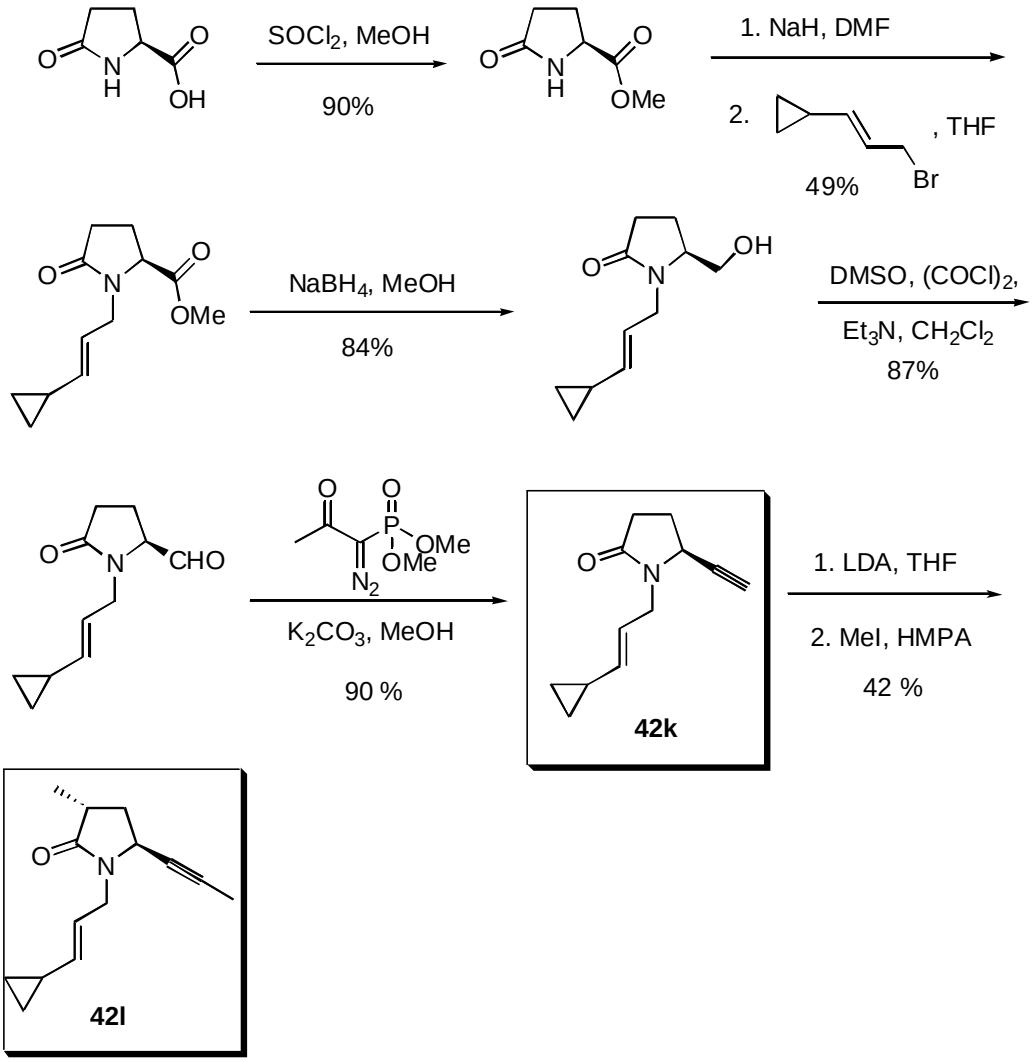
$CDCl_3$): δ 7.67 (d, *J*=8.5 Hz, 2H), 7.23 (d, *J*=8.5 Hz, 2H), 5.27 (dt, *J*=7.0, 15.0 Hz, 1H), 5.16 (dd, *J*=8.5, 15.0 Hz, 1H), 4.05 (s, 2H), 3.67 (d, *J*=6.5 Hz, 1H), 2.37 (s, 3H), 1.81 (m, 2H), 1.60 (m, 2H), 1.23 (m, 2H), 1.17 (m, 3H), 0.87 (m, 2H), -0.06 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 143.2, 141.1, 136.1, 129.4, 127.7, 118.9, 98.2, 88.7, 48.3, 39.0, 36.5, 26.4, 23.06, 21.3, 19.9, -0.35; HRMS (EI+) Calc'd for $C_{23}H_{33}NO_2SSi$: 415.2001. Found: 415.2009.
nOe study:

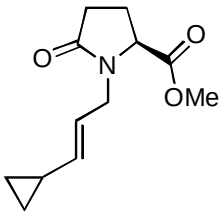


δ_a = 5.16 ppm
δ_b = 0.87 ppm

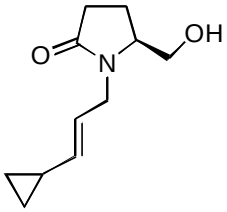
42j

42k, **42l**:



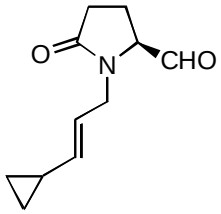


1-(3-Cyclopropylallyl)-5-oxo-pyrrolidine-2-carboxylic acid methyl ester: To a solution of 3-cyclopropyl-1-propenol (455 mg, 4.64 mmol) in 6 mL of distilled THF was added *n*-butyllithium (1.45 M in hexane, 3.7 mL, 5.4 mmol) at −78°C. After stirring for 20 min at −78 °C, to this solution was added methanesulfonyl chloride (576 mg, 0.39 mL, 5.03 mmol) followed by the addition of 100 mg of anhydrous lithium bromide at the same temperature. This solution was stirred at −78°C for 2 h and then −10°C for 5 min to generate the allylbromide solution *in situ*. In another flask containing sodium hydride (60% in mineral oil, 201 mg, 5.03 mmol) at 0°C was added 2 mL of DMF followed by the addition of a solution of 1-(3-cyclopropylallyl)-5-oxo-pyrrolidine-2-carboxylic acid methyl ester (553 mg, 3.87 mmol) in 4 mL of distilled DMF. The resulting solution was stirred at 0°C for 1 h before the mixture was treated dropwise with the allylbromide solution generated *in situ* at 0°C. The resulting solution was heated at 50°C for 1 min and then rt for 16 h. The solution was then concentrated *in vacuo*. The residue was then submitted to silica gel chromatography eluting with 10%-75% diethyl ether in petroleum ether to afford 1-(3-cyclopropylallyl)-5-oxo-pyrrolidine-2-carboxylic acid methyl ester (360 mg, 1.85 mmol, 49 %) as a pale yellow oil.
IR (film) cm^{-1}: 3005w, 2955m, 1743s, 1694s, 1437m, 1416m, 1381w, 1352w, 1280m, 1206m, 1176m, 1046w, 1024w, 966m, 813w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.37 (ddd, *J*=6.0, 8.0, 15.0 Hz, 1H), 5.11 (ddd, *J*=1.0, 8.5, 15.0 Hz, 1H), 4.20 (ddd, *J*=1.5, 6.0, 15.0 Hz, 1H), 4.16 (dd, *J*=3.0, 9.0 Hz, 1H), 3.74 (s, 3H), 3.51 (dd, *J*=8.0, 13.5 Hz, 1H), 2.52 (dtd, *J*=1.0, 9.0, 16.5 Hz, 1H), 2.36 (m, 2H), 2.05 (m, 1H), 1.37 (m, 1H), 0.70 (m, 2H), 0.36 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 174.7, 172.5, 139.7, 120.7, 58.8, 52.3, 43.6, 29.6, 22.8, 13.3, 6.74, 6.66; HRMS (EI+) Calc'd for $C_{12}H_{17}NO_3$: 223.1208. Found: 223.1210.

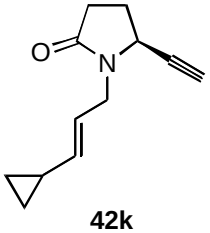


1-(3-Cyclopropylallyl)-5-hydroxymethylpyrroloidin-2-one: To a solution of 1-(3-cyclopropylallyl)-5-oxo-pyrrolidine-2-carboxylic acid methyl ester (146 mg, 0.65 mmol) in 2 mL of distilled methanol was added sodium borohydride (25 mg, 0.65 mmol) at 0°C. The reaction mixture was warmed to rt and stirred overnight. After the addition of three drops of concentrated HCl, the solvent was removed *in vacuo* and the residue was submitted to flash chromatography eluting with 50% ethyl acetate in petroleum ether to 25% methanol in ethyl acetate to yield 1-(3-cyclopropylallyl)-5-hydroxymethylpyrroloidin-2-one (79 mg, 0.41 mmol, 63% (84% brsm)) and 35 mg of the starting ester.
IR (film) cm^{-1}: 3390b, 3004w, 2932w, 1662s, 1458m, 1422m, 1380w, 1349w, 1279w, 1247w, 1191w, 1156w, 1091w, 1051w, 1018w, 965m, 813w, 668w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.40 (ddd, *J*=5.5, 8.0, 15.0 Hz, 1H), 5.16 (ddd, *J*=1.5, 8.5, 15.0 Hz, 1H), 4.18 (m, 1H), 3.76 (m, 1H),

3.67 (m, 1H), 3.61 (m, 1H), 3.51 (m, 2H), 2.46 (m, 1H), 2.29 (m, 1H), 2.07 (m, 1H), 2.01 (m, 1H), 1.35 (m, 1H), 0.69 (m, 2H), 0.34 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 175.6, 138.6, 121.4, 62.0, 58.7, 42.4, 30.6, 20.9, 13.3, 6.71; HRMS (EI+) Calc'd for $C_{11}H_{17}NO_2$: 195.1259. Found: 195.1260.

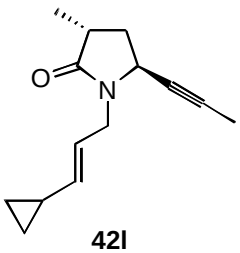


1-(3-Cyclopropyl-allyl)-5-oxo-pyrrolidine-2-carboxylaldehyde: To a solution of oxallyl chloride (57 mg, 39 uL, 0.45 mmol) in 0.5 mL of distilled dichloromethane was added DMSO (67 mg, 61 uL, 0.86 mmol) at -78°C. The resulting mixture was stirred at -78 °C for 30 min. To this solution was added 1-(3-cyclopropylallyl)-5-hydroxymethylpyrroloidin-2-one (79 mg, 0.41 mmol) in 1.5 mL of dichloromethane at -78 °C. After 30 min, to this mixture was added triethylamine (124 mg, 171 uL, 1.23 mmol). The mixture was slowly warmed to rt and stirred overnight. Without workup, column chromatography eluting with 50% ethyl acetate in petroleum ether to 20% methanol in petroleum ether afforded 1-(3-cyclopropyl-allyl)-5-oxo-pyrrolidine-2-carboxylaldehyde (20 mg, 0.10 mmol, 25%) as a pale brown oil.
IR (film) cm^{-1}: 2966w, 2932w, 1694s, 1418m, 1229m, 964m, 813w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.52 (d, *J*=2.7 Hz, 1H), 5.38 (dd, *J*=7.5, 15.5 Hz, 1H), 5.12 (dd, *J*=8.7, 15.5 Hz, 1H), 4.52 (m, 1H), 4.16 (m, 1H), 3.66 (m, 1H), 1.88-2.58 (m, 4H), 1.30 (m, 1H), 0.66 (m, 2H), 0.31 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) of two rotamers: δ 198.8, 176.2, 176.1, 138.6, 138.4, 121.6, 121.5, 60.9, 60.7, 55.03, 54.96, 43.8, 43.3, 30.3, 30.1, 19.0, 18.6, 6.62, 6.54; HRMS (EI+) Calc'd for $C_{11}H_{15}NO_2$: 193.1103. Found: 193.1102.



42k

1-(3-Cyclopropyl-allyl)-5-ethynyl-pyrrolidin-2-one (**42k**): To a solution of 1-(3-cyclopropyl-allyl)-5-oxo-pyrrolidine-2-carboxylaldehyde (20 mg, 0.10 mmol) in 0.5 mL of methanol were added potassium carbonate (41 mg, 0.30 mmol) and ethyl dizaoacetylphosphonate (29 mg, 0.15 mmol) at rt. The mixture was stirred overnight. Without futher workup, flash column eluting with 50% diethyl ether in petroleum ether afforded alkyne **42k** (17 mg, 0.090 mmol, 90%) as a pale yellow oil.
IR (film) cm^{-1}: 3293m, 3226m, 3082w, 3004m, 2920m, 2113w, 1691s, 1440s, 1414s, 1380w, 1349m, 1314w, 1279w, 1235m, 1191w, 1152w, 1049w, 1022w, 964s, 853w, 813w, 668w; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 5.26 (ddd, *J*=5.0, 8.2, 15.2 Hz, 1H), 5.20 (dd, *J*=8.2, 15.6 Hz, 1H), 4.29 (m, 2H), 3.46 (dd, *J*=8.2, 14.6 Hz, 1H), 2.00-2.68 (m, 4H), 1.86 (s, 1H), 1.34 (m, 1H), 0.71 (m, 2H), 0.37 (m, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ 173.8, 139.5, 120.7, 81.5, 73.2, 48.0, 42.3, 30.0, 25.7, 13.2, 6.66, 6.54; HRMS (EI+) Calc'd for $C_{12}H_{15}NO$: 189.1154. Found: 189.1158.

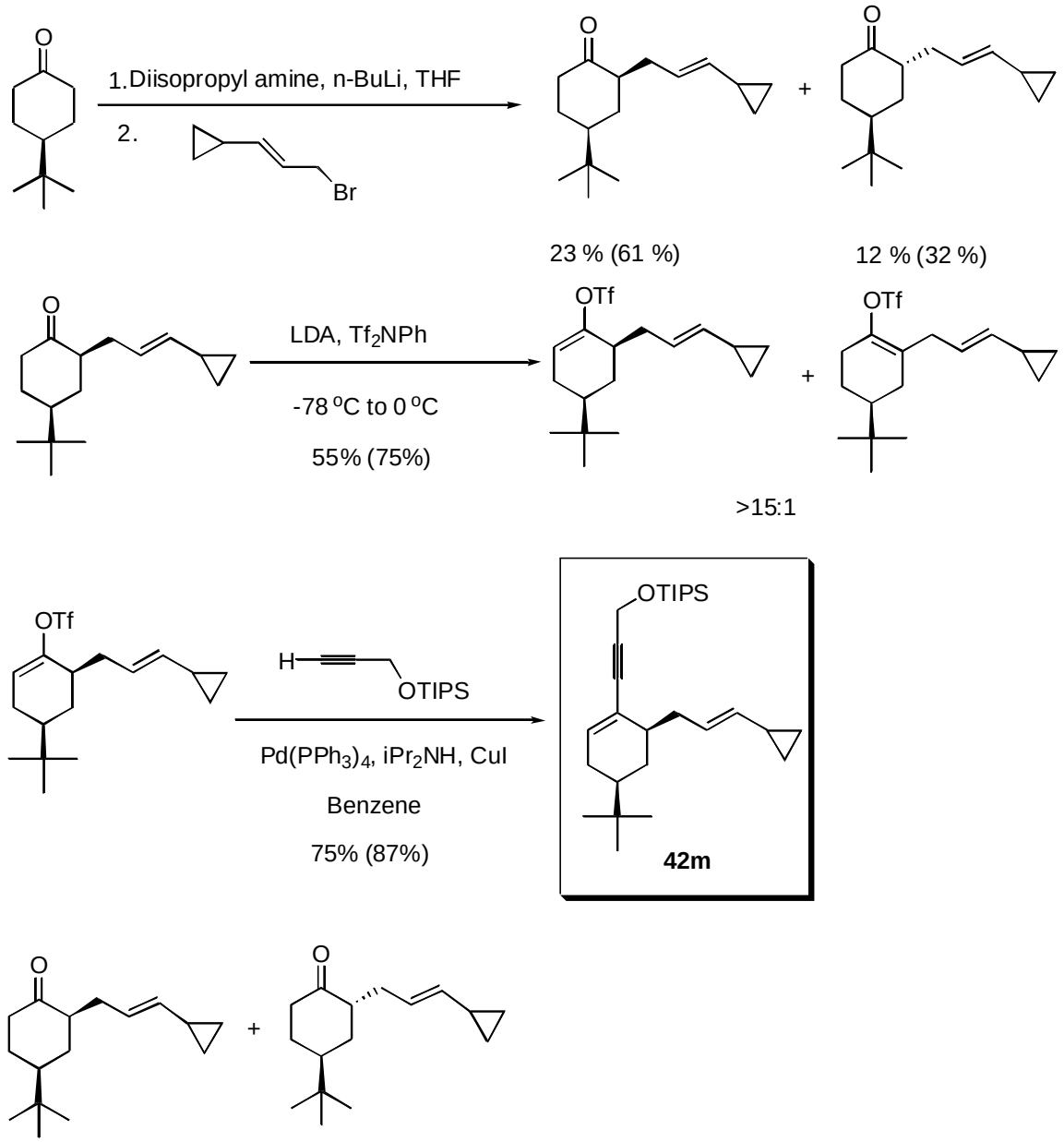


42l

1-(3-Cyclopropyl-allyl)-3,5-*trans*-3-methyl-5-prop-1-ynyl-pyrrolidin-2-one (42l): To a solution of diisopropylamine (61 mg, 84 ul, 0.60 mmol) in 1.0 mL of distilled THF was added *n*-butyllithium (1.43 M in hexane, 0.46 mL, 0.66 mmol) at -78°C. The solution was then stirred at rt for 30 min before the solution at -78°C was cannulated into a flask containing lactam **42k** (54 mg, 0.29 mmol). Upon the addition of LDA, the reaction mixture turned dark orange. At -78 °C, this solution was stirred for an additional 2 h and to the resulting solution was added methyl iodide (203 mg, 89 ul, 1.43 mmol) followed by the addition of HMPA (100 ul, 0.57 mmol). The reaction mixture was kept at -78°C for 2h and warmed to 0°C. To the mixture was added 4 drops of water. After the removal of solvent *in vacuo*, flash chromatography of the crude reaction mixture eluting with 20%-75% diethyl ether in petroleum ether afforded **42l** (26 mg, 0.12 mmol, 42%) as a colorless oil.

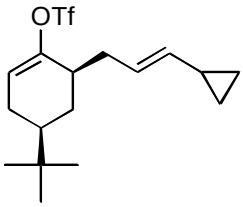
IR (film) cm^{-1}: 3082w, 2966w, 2932w, 2874w, 1694s, 1417s, 1379w, 1346m, 1307w, 1228m, 1204w, 1112w, 1048w, 1021w, 964m, 854w, 813w, 786w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.39 (ddd, *J*=5.1, 8.4, 15.5 Hz, 1H), 5.17 (dd, *J*=8.7, 15.5 Hz, 1H), 4.28 (ddd, *J*=1.2, 5.1, 14.7 Hz, 1H), 4.17 (dt, *J*=2.1, 8.1 Hz, 1H), 3.40 (dd, *J*=8.4, 14.7 Hz, 1H), 2.61 (dd, *J*=7.8, 15.5 Hz, 1H), 2.23 (ddd, *J*=2.4, 8.1, 12.0 Hz, 1H), 1.85 (m, 2H), 1.80 (d, *J*=2.1 Hz, 3H), 1.36 (m, 1H), 1.17 (d, *J*=7.5 Hz, 3H), 0.69 (m, 2H), 0.36 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 176.3, 138.8, 121.3, 80.4, 72.6, 46.6, 42.6, 35.6, 35.2, 15.8, 13.3, 6.77, 6.65, 3.43; HRM Calc'd for $C_{14}H_{19}NO$: 217.1467. Found: 217.1472.

42m:

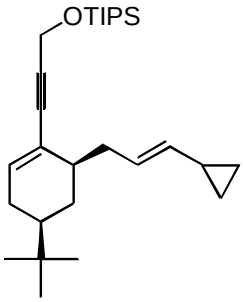


(*2R*,4S)-2,4-*cis*-4-*tert*-Butyl-2-(3-cyclopropyl-allyl)-cyclohexanone** and **(*2R*,4R**)-2,4-*trans*-4-*tert*-Butyl-2-(3-cyclopropyl-allyl)-cyclohexanone**: To a solution of diisopropyl amine (56 mg, 77 uL, 0.55 mmol) in 0.5 mL of distilled THF was added *n*-butyllithium (1.6 M in hexane, 0.34 mL, 0.55 mmol) at −78 °C. The resulting light yellow solution was stirred at – 78 °C for 10 min and then 0 °C for 30 min. To this LDA solution was added a solution of 4*tert*-butyl cyclohexanone in 0.5 mL of distilled THF at −78 °C. This solution was stirred at −78 °C for 1h. To allylic bromide (0.46 mmol, generated *in situ*) that was prepared following the procedure described in V-19 was added the ketone enolate solution formed at −78 °C. The solution was warmed to rt overnight. After the removal of solvent *in vacuo*, purification by flash chromatography afforded (*2R*,4S**)-2,4-*cis*-4-*tert*-butyl-2-(3-cyclopropyl-allyl)-cyclohexanone (25 mg, 0.11 mmol, 23% (61% brsm)) and (*2R*,4R**)-2,4-*trans*-4-*tert*-butyl-2-(3-cyclopropyl-

allyl)-cyclohexanone (13 mg, 0.056 mmol, 12% (32% brsm)) as colorless oils. The two isomers were isolated separately and their structures were determined by later derivatizations.
IR (film) cm^{-1} for (*2R*,4S**)-2,4-*cis*-4-*tert*-butyl-2-(3-cyclopropyl-allyl)-cyclohexanone: 3082w, 2958s, 2869s, 1716s, 1480w, 1446w, 1395w, 1366m, 1228w, 1179w, 1045w, 1019w, 963m, 810w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.48 (dt, *J*=7.2, 15.3 Hz, 1H), 4.97 (dd, *J*=8.4, 15.3 Hz, 1H), 1.03-2.51 (m, 11H), 0.90 (s, 9H), 0.65 (m, 2H), 0.29 (m, 2H). IR (film) cm^{-1} for (*2R*,4R**)-2,4-*trans*-4-*tert*-butyl-2-(3-cyclopropyl-allyl)-cyclohexanone: 3082w, 3005m, 2957s, 2869s, 1713s, 1686w, 1478w, 1444w, 1367m, 1230w, 1020w, 961m, 810w; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.36 (dt, *J*=6.9, 15.3 Hz, 1H), 4.99 (dd, *J*=7.8, 15.3 Hz, 1H), 2.32 (m, 4H), 2.17 (m, 1H), 1.99 (m, 1H), 1.87 (m, 1H), 1.48 (m, 4H), 0.89 (s, 9H), 0.66 (m, 2H), 0.30 (m, 2H); HRMS (EI+) Calc'd for $C_{16}H_{26}O$ $[M]^+$: 234.1984. Found: 234.1984.



Trifluoromethanesulfonic acid 4-*tert*-butyl-6-(3-cyclopropylallyl)-1-cyclohexenyl ester: To a solution of diisopropylamine (54 mg, 0.53 mmol) in 1 mL of distilled THF was added n-butyllithium solution in hexane (0.38 mL, 0.57 mmol, 1.49 M) at –78 °C. After the addition, the solution was warmed to 0 °C and stirred for 0.5 hr. To above pale yellow solution was added N-phenylbistrifluoromethanesulfonamide at –78 °C followed by the slow addition of (*2R*,4S**)-2,4-*cis*-4-*tert*-butyl-2-(3-cyclopropyl-allyl)-cyclohexanone (100 mg, 0.43 mmol) in 1 mL of distilled THF at the same temperature over 15 min. The solution was stirred at –78 °C for 1.5 hrs before it was stirred at 0 °C overnight. After removal of the solvent in vacuo, flash chromatography of the reaction mixture residue afforded trifluoromethanesulfonic acid 4-*tert*-butyl-6-(3-cyclopropylallyl)-1-cyclohexenyl ester as a colorless oil (81 mg, 0.24 mmol, 55 % and 75 % brsm, only one isomer was obtained based on NMR analysis).
^{1}H-NMR (200 MHz, $CDCl_3$): δ 5.77 (m, 1H), 5.41 (dt, J=7.2, 15.2 Hz, 1H), 5.03 (dd, J=8.2, 15.2 Hz, 1H), 2.8 (m, 1H), 2.55 (m, 1H), 2.34 (m, 1H), 2.13 (m, 2H), 1.92 (m, 2H), 1.31 (m, 2H), 0.88 (s, 9H), 0.68 (m, 2H), 0.34 (m, 2H).



42m

(*4R*,6R)-{3-[4,6-*cis*-4-*tert*-Butyl-6-(3-cyclopropyl-allyl)-cyclohex-1-enyl]-prop-2-ynyloxy}-tri-isopropyl silane** (**42m**): At rt a solution of trifluoromethanesulfonic acid 4-*tert*-butyl-6-(3-cyclopropylallyl)-1-cyclohexenyl ester (75 mg, 0.20 mmol, a mixtutre of two isomers with a ratio of 6.5 to 1 as shown in the scheme above) and palladium tetrakistriphenylphosphine (12

mg, 0.01 mmol) in benzene (0.5 mL) was stirred for 10 min to give an orange solution. To this solution was treated successively with a 0.5 mL of benzene solution of alkyne (42 mg, 0.20 mmol), diisopropylamine (61 mg, 84 uL, 0.60 mmol) and cuprous iodide (19 mg, 0.10 mmol) at rt. Following the addition of cuprous iodide, the solution turned dark brown. After stirring for 4 h, the solution was concentrated *in vacuo* before the residue was submitted to flash chromatography eluting with pure petroleum ether to 2 % diethyl ether in petroleum ether to give **42m** (65 mg, 0.15 mmol, 75%) as a colorless oil and starting material (10 mg, 0.03 mmol, 15%). IR (film) cm^{-1}: 2944s, 2867s, 1465m, 1366m, 1259w, 1211w, 1095s, 1068m, 1015w, 997w, 961w, 920w, 882m, 769w, 683m; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.16 (m, 1H), 5.50 (dt, *J*=7.0, 15.5 Hz, 1H), 5.02 (dd, *J*=8.5, 15.5 Hz, 1H), 4.53 (s, 2H), 2.53 (m, 1H), 2.10 (m, 3H), 1.86 (m, 2H), 1.38 (m, 3H), 1.09 (m, 21 H), 0.87 (m, 9H), 0.68 (m, 2H), 0.32 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 136.4, 135.6, 125.5, 124.4, 87.2, 84.8, 52.4, 43.4, 39.4, 37.4, 32.2, 30.0, 27.7, 27.1, 18.0, 17.95, 17.86, 13.6, 12.0, 11.9, 6.41, 6.40; HRMS (EI+) Calc'd for $C_{28}H_{48}SiO$ $[M]^+$: 428.3474. Found: 428.3468.

Part III:
X-Ray Data for 6ee:

X-Ray report for **6ee:**
Data Collection

A colorless plate crystal of $C_{14}H_{24}O_2Si$ having approximate dimensions of 0.44 x 0.25 x 0.04 mm was mounted on a quartz fiber using Paratone N hydrocarbon oil. All measurements were made on a Bruker-Siemens SMART[1] CCD area detector with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the measured positions of 1865 reflections in the range $4.95^o < 2\theta < 48.41^o$ corresponded to a primitive monoclinic cell with dimensions:

a = 14.873(2) Å
b = 9.940(2) Å β = 100.006(3)°
c = 10.143(3) Å
V = 1476.8(5) Å^3

For Z = 4 and F.W. = 252.43, the calculated density is 1.14 g/cm^3. The systematic absences of:

h0l: l ± 2n
0k0: k ± 2n

uniquely determine the space group to be:

$P2_1/c$ (#14)

The data were collected at a temperature of -120 ± 1°C using the ω scan technique to a maximum 2θ value of 49.5°. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3°, counted for a total of 10 seconds per frame.

Data Reduction

Data were integrated by the program SAINT[2] with box parameters of 1.6 X 1.6 X 0.6°. Equivalent reflections were merged. Of the 6624 reflections which were collected, 2442 were unique (R_{int} = 0.065). No decay correction was applied.

The linear absorption coefficient, μ, for Mo-Kα radiation is 1.5 cm^{-1}. Data were analyzed for agreement and possible absorption using SADABS[3]. A semi-empirical absorption correction based on 2627 reflections with $I > 5\sigma(I)$ was applied that resulted in apparent transmission factors ranging from 0.26 to 1.0. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[4] and expanded using Fourier techniques[5]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by difference Fourier synthesis and were constrained to idealized geometries in a riding (AFIX) refinement. A single free rotation angle about the C–CH_3 or C–OH bond vector was also refined in the case of methyl and hydroxyl groups. The final cycle of full-matrix least-squares refinement[6] on F^2 was based on 2442 observed reflections and 160 variable parameters and converged (largest parameter shift was less than 1% of its esd) with unweighted and weighted agreement factors of:

$$R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o| = 0.050 \text{ (1531 refl., } F_o > 4\sigma(F_o))$$

$$wR_2 = [\, \Sigma \, (\, w \, (F_o^{\,2} - F_c^{\,2})^2 \,) / \, \Sigma \, w(F_o^{\,2})^2 \,]^{1/2} = 0.128 \text{ (all data)}$$

The standard deviation of an observation of unit weight (S)[7] was 0.94. The weighting scheme was that of Sheldrick;[4] weights were refined to convergence. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and -0.32 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[8]. Anomalous dispersion effects were included in F_c[9]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[10]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[11]. All calculations were performed using the CrystalStructure[12,13] crystallographic software package except for refinement, which was performed using SHELXL-97[4].

References

(1) SMART: Area-Detector Software Package,
Siemens Industrial Automation, Inc.: Madison, WI (1995)

(2) SAINT: SAX Area-Detector Integration Program, V4.024;

Siemens Industrial Automation, Inc.: Madison, WI (1995)

(3) SADABS: (v 5.04) Part of the SHELXTL Crystal Structure Determination, Siemens Industrial Automation, Inc.: Madison, WI (1998)

(4) SHELX97: Sheldrick, G.M. (1997).

(5) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(6) Least Squares function minimized: (SHELXL97)

$$\Sigma w(F_o^2-F_c^2)^2 \quad \text{where } w = 1 / [\sigma^2(F_o^2) + (0.0693\ P)^2]$$
$$P = (F_o^2 + 2F_c^2) / 3 \text{ for } F_o^2 >= 0;\ 2F_c^2 / 3 \text{ for } F_o^2 < 0$$

(7) Standard deviation of an observation of unit weight:

$$S = [\Sigma w(F_o^2-F_c^2)^2/(N_O-N_V)]^{1/2}$$

where: N_O = number of observations; N_V = number of variables

(8) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(9) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(10) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(11) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(12) CrystalStructure 2.00: Crystal Structure Analysis Package, Rigaku and MSC (2001).

(13) CRYSTALS Issue 10: Watkin, D.J., Prout, C.K. Carruthers, J.R. & Betteridge, P.W. Chemical Crystallography Laboratory, Oxford, UK.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{14}H_{24}O_2Si$
Formula Weight	252.43
Crystal Color, Habit	colorless plate
Crystal Dimensions	0.44 X 0.25 X 0.04 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	1865 ($4.95^o < 2\theta < 48.41^o$)
Lattice Parameters	a = 14.873(2) Å b = 9.940(2) Å c = 10.143(3) Å β = 100.006(3) ^{o} V = 1476.8(5) $Å^3$
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.135 g/cm^3
F_{000}	552.00
μ(MoKα)	1.49 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker-Siemens SMART CCD
Radiation	MoKα (λ = 0.71073 Å) graphite monochromated
Temperature	-120°C
Scan Type	ω(0.3°/frame)
Scan Rate	10 sec Frame Exposure
$2\theta_{max}$	49.5°
No. of Reflections Measured	Total: 6624 Unique: 2442 (R_{int} = 0.065)
Corrections	Absorption, Lorentz, polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\, w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1/ [\, \sigma^2(F_o^2) + (0.0693 \cdot P)^2]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations	2442
No. Variables	160
Reflection/Parameter Ratio	15.26
Residuals: R_1; wR_2	0.050 (1531 refl., $F_o > 4\sigma(F_o)$); 0.128 (all data)
Goodness of Fit Indicator (S)	0.94
Max Shift/Error in Final Cycle	< 1%
Maximum peak in Final Diff. Map	0.34 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.32 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Si1	0.83509(5)	0.06504(8)	0.72957(8)	0.0288(3)
O1	0.60659(12)	0.00574(19)	0.66462(16)	0.0276(5)
H1	0.5638	0.0620	0.6524	0.041
O2	0.54347(14)	-0.3543(2)	0.9429(2)	0.0437(6)
H2	0.5644	-0.3928	1.0154	0.066
C1	0.78994(18)	-0.0901(3)	0.8025(2)	0.0238(7)
C2	0.86519(18)	-0.1958(3)	0.8402(3)	0.0273(7)
H2A	0.9250	-0.1543	0.8353	0.033
H2B	0.8662	-0.2245	0.9339	0.033
C3	0.8523(2)	-0.3196(3)	0.7496(3)	0.0344(8)
H3A	0.9042	-0.3813	0.7787	0.041
H3B	0.8558	-0.2903	0.6574	0.041
C4	0.7659(2)	-0.3974(3)	0.7452(3)	0.0375(8)
H4	0.7595	-0.4747	0.6894	0.045
C5	0.6971(2)	-0.3727(3)	0.8091(3)	0.0331(8)
H5	0.6483	-0.4357	0.7972	0.040
C6	0.68909(18)	-0.2539(3)	0.8988(3)	0.0244(7)
H6	0.7339	-0.2642	0.9839	0.029
C7	0.59342(19)	-0.2335(3)	0.9318(3)	0.0311(7)
H7	0.5987	-0.1822	1.0177	0.037
C8	0.54575(17)	-0.1459(3)	0.8184(3)	0.0290(7)
H8A	0.5268	-0.1994	0.7359	0.035
H8B	0.4914	-0.1014	0.8429	0.035
C9	0.61887(17)	-0.0430(3)	0.7999(2)	0.0224(7)
C10	0.70795(18)	-0.1217(3)	0.8306(2)	0.0208(6)
C11	0.61875(19)	0.0757(3)	0.8960(3)	0.0308(7)
H11A	0.6685	0.1374	0.8862	0.046
H11B	0.6273	0.0424	0.9883	0.046
H11C	0.5603	0.1233	0.8751	0.046
C12	0.7580(2)	0.2016(3)	0.6553(4)	0.0571(11)
H12A	0.7943	0.2763	0.6296	0.086
H12B	0.7217	0.2331	0.7211	0.086
H12C	0.7172	0.1677	0.5759	0.086
C13	0.9175(2)	0.1411(3)	0.8702(3)	0.0496(9)
H13A	0.9417	0.2252	0.8400	0.074
H13B	0.9679	0.0782	0.8987	0.074
H13C	0.8862	0.1596	0.9456	0.074
C14	0.8981(2)	0.0120(3)	0.5952(3)	0.0368(8)
H14A	0.8552	-0.0262	0.5203	0.055
H14B	0.9438	-0.0559	0.6304	0.055
H14C	0.9287	0.0902	0.5639	0.055

$B_{eq} = 8/300\,\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si1	0.0313(5)	0.0243(5)	0.0311(5)	0.0024(4)	0.0064(4)	-0.0022(4)
O1	0.0319(12)	0.0279(12)	0.0203(10)	0.0061(8)	-0.0034(8)	0.0050(9)
O2	0.0392(13)	0.0441(14)	0.0414(14)	0.0218(10)	-0.0113(10)	-0.0228(11)
C1	0.0293(16)	0.0229(16)	0.0179(15)	0.0005(12)	0.0002(12)	0.0007(13)
C2	0.0296(16)	0.0311(17)	0.0201(15)	0.0047(13)	0.0008(13)	0.0044(14)
C3	0.044(2)	0.0336(19)	0.0235(17)	0.0028(13)	-0.0007(14)	0.0152(16)
C4	0.056(2)	0.0222(18)	0.0284(17)	-0.0053(13)	-0.0104(16)	0.0083(16)
C5	0.0432(19)	0.0186(16)	0.0311(18)	0.0021(13)	-0.0113(15)	-0.0036(15)
C6	0.0297(16)	0.0196(15)	0.0201(15)	0.0036(12)	-0.0066(12)	-0.0024(13)
C7	0.0330(18)	0.0335(18)	0.0243(16)	0.0070(13)	-0.0023(13)	-0.0132(14)
C8	0.0242(16)	0.0321(18)	0.0280(17)	0.0045(13)	-0.0031(13)	-0.0019(14)
C9	0.0258(16)	0.0221(16)	0.0174(15)	0.0032(12)	-0.0020(12)	-0.0005(13)
C10	0.0269(16)	0.0199(15)	0.0136(14)	-0.0008(11)	-0.0019(12)	-0.0004(13)
C11	0.0360(17)	0.0296(17)	0.0248(16)	-0.0027(13)	-0.0002(13)	0.0061(14)
C12	0.054(2)	0.032(2)	0.090(3)	0.0284(19)	0.024(2)	0.0047(18)
C13	0.059(2)	0.050(2)	0.042(2)	-0.0144(17)	0.0132(17)	-0.0214(19)
C14	0.0438(19)	0.038(2)	0.0296(17)	-0.0009(15)	0.0089(14)	-0.0114(15)

The general temperature factor expression:
$\exp\{-2\pi^2[(a^*)^2 2U_{11}h^2 + (b^*)^2 U_{22}k^2 + (c^*)^2 U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl]\}$

Table 3. Bond Lengths (Å)

atom1	atom2	distance
Si1	C12	1.850(3)
Si1	C14	1.860(3)
Si1	C1	1.884(3)
Si1	C13	1.871(3)
O1	C9	1.437(3)
O1	H1	0.8400
O2	C7	1.427(3)
O2	H2	0.8400
C1	C10	1.337(3)
C1	C2	1.534(4)
C2	C3	1.527(4)
C2	H2A	0.9900
C2	H2B	0.9900
C3	C4	1.493(4)
C3	H3A	0.9900
C3	H3B	0.9900
C4	C5	1.326(4)
C4	H4	0.9500
C5	C6	1.508(4)
C5	H5	0.9500
C6	C7	1.531(4)
C6	C10	1.533(4)
C6	H6	1.0000
C7	C8	1.517(4)
C7	H7	1.0000
C8	C9	1.528(4)
C8	H8A	0.9900
C8	H8B	0.9900
C9	C10	1.523(4)
C9	C11	1.531(4)
C11	H11A	0.9800
C11	H11B	0.9800
C11	H11C	0.9800
C12	H12A	0.9800
C12	H12B	0.9800
C12	H12C	0.9800
C13	H13A	0.9800
C13	H13B	0.9800
C13	H13C	0.9800
C14	H14A	0.9800
C14	H14B	0.9800
C14	H14C	0.9800

Table 4. Bond Angles(º)

atom1	atom2	atom3	angle
C12	Si1	C14	105.38(15)
C12	Si1	C1	121.50(13)
C14	Si1	C1	108.36(13)
C12	Si1	C13	106.95(17)
C14	Si1	C13	109.03(15)
C1	Si1	C13	105.22(13)
C9	O1	H1	109.5
C7	O2	H2	109.5
C10	C1	C2	116.0(2)
C10	C1	Si1	132.6(2)
C2	C1	Si1	111.37(18)
C3	C2	C1	113.0(2)
C3	C2	H2A	109.0
C1	C2	H2A	109.0
C3	C2	H2B	109.0
C1	C2	H2B	109.0
H2A	C2	H2B	107.8
C2	C3	C4	116.9(2)
C2	C3	H3A	108.1
C4	C3	H3A	108.1
C2	C3	H3B	108.1
C4	C3	H3B	108.1
H3A	C3	H3B	107.3
C5	C4	C3	128.5(3)
C5	C4	H4	115.7
C3	C4	H4	115.7
C4	C5	C6	126.0(3)
C4	C5	H5	117.0
C6	C5	H5	117.0
C7	C6	C5	114.2(2)
C7	C6	C10	103.6(2)
C5	C6	C10	111.1(2)
C7	C6	H6	109.3
C5	C6	H6	109.3
C10	C6	H6	109.3
O2	C7	C6	115.0(2)
O2	C7	C8	111.2(2)
C6	C7	C8	103.8(2)
O2	C7	H7	108.9
C6	C7	H7	108.9
C8	C7	H7	108.9
C9	C8	C7	103.2(2)
C9	C8	H8A	111.1
C7	C8	H8A	111.1
C9	C8	H8B	111.1
C7	C8	H8B	111.1
H8A	C8	H8B	109.1
O1	C9	C10	109.3(2)
O1	C9	C8	111.6(2)
C10	C9	C8	104.1(2)
O1	C9	C11	109.5(2)
C10	C9	C11	111.3(2)
C8	C9	C11	111.0(2)
C1	C10	C6	122.9(2)
C1	C10	C9	129.0(2)
C6	C10	C9	108.2(2)
C9	C11	H11A	109.5
C9	C11	H11B	109.5
H11A	C11	H11B	109.5
C9	C11	H11C	109.5
H11A	C11	H11C	109.5
H11B	C11	H11C	109.5
Si1	C12	H12A	109.5
Si1	C12	H12B	109.5
H12A	C12	H12B	109.5
Si1	C12	H12C	109.5
H12A	C12	H12C	109.5
H12B	C12	H12C	109.5
Si1	C13	H13A	109.5
Si1	C13	H13B	109.5
H13A	C13	H13B	109.5
Si1	C13	H13C	109.5
H13A	C13	H13C	109.5
H13B	C13	H13C	109.5
Si1	C14	H14A	109.5
Si1	C14	H14B	109.5
H14A	C14	H14B	109.5
Si1	C14	H14C	109.5
H14A	C14	H14C	109.5
H14B	C14	H14C	109.5

Table 5. Torsion Angles(º)

atom1	atom2	atom3	atom4	angle
C12	Si1	C1	C10	-10.3(3)
C14	Si1	C1	C10	-132.4(3)
C13	Si1	C1	C10	111.1(3)
C12	Si1	C1	C2	172.4(2)
C14	Si1	C1	C2	50.3(2)
C13	Si1	C1	C2	-66.2(2)
C10	C1	C2	C3	72.0(3)
Si1	C1	C2	C3	-110.3(2)
C1	C2	C3	C4	-59.5(3)
C2	C3	C4	C5	0.9(4)
C3	C4	C5	C6	2.6(5)
C4	C5	C6	C7	166.2(3)
C4	C5	C6	C10	49.5(4)
C5	C6	C7	O2	33.7(3)
C10	C6	C7	O2	154.6(2)
C5	C6	C7	C8	-88.0(3)
C10	C6	C7	C8	32.9(3)
O2	C7	C8	C9	-166.3(2)
C6	C7	C8	C9	-42.1(3)
C7	C8	C9	O1	152.0(2)
C7	C8	C9	C10	34.3(3)
C7	C8	C9	C11	-85.5(3)
C2	C1	C10	C6	1.1(4)
Si1	C1	C10	C6	-176.14(19)
C2	C1	C10	C9	-176.6(2)
Si1	C1	C10	C9	6.2(4)
C7	C6	C10	C1	170.3(2)
C5	C6	C10	C1	-66.7(3)
C7	C6	C10	C9	-11.6(3)
C5	C6	C10	C9	111.4(2)
O1	C9	C10	C1	44.8(4)
C8	C9	C10	C1	164.0(3)
C11	C9	C10	C1	-76.3(3)
O1	C9	C10	C6	-133.2(2)
C8	C9	C10	C6	-13.9(3)
C11	C9	C10	C6	105.7(2)